Supplementary Information

Asymmetric total synthesis of humulane sesquiterpenoids alashanoids B, C, E, F and 2,9-humuladien-6-ol-8-one

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1. General Information:

All moisture or oxygen-sensitive reactions were carried out under an argon atmosphere in oven flasks. The solvents were purified by distillation over the drying agents indicated and were transferred under argon: toluene, THF and Et_2O from Na; MeOH from Mg and I_2; CH_2Cl_2, Et_3N and DMF from CaH_2. All reactions were monitored by thin-layer chromatography (TLC) on silica gel GF254 plates using UV light as visualizing agent (if applicable), and a solution of Anisal in EtOH followed by heating as developing agents. The products were purified by flash column chromatography. Bruker AM 400 MHz instrument or 600 MHz,500 MHz NMR instrument. Chemical shifts were denoted in ppm (δ), and calibrated by using residual undeuterated solvent ($CDCl_3$ (7.26 ppm), ^1H **NMR** and the deuterated solvent ($CDCl_3$ (77.00 ppm), as internal standard for **^{13}C NMR**. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, dd = double doublet, td = triple doublet, dt =double triplet, m = multiplet. The high-resolution mass spectral analysis (**HRMS**) data were measured on Thermo Fisher Orbitrap Elite Mass Spectrometer or a LCT Premier XE (Waters) mass spectrometer (Waters, Milford, MA, U.S.) by means of the ESI technique. Electron ionization mass spectra (**EI-MS**) were measured on a Shimadzu GCMSQP2010SE spectrometer by direct inlet at 70 eV and the corresponding signals were given in m/z with relative intensity (%) in brackets. The **IR** spectra were recorded on Nicolet Nexus 670 FT-IR spectrometer. **UV** and **ECD** data were detected on a Shimadzu UV-2450 spectrophotometer and a JASCO J-815 spectrometer and polarimeter respectively. The **X-ray** single-crystal determination was performed on an Agilent Super Nova single crystal X-ray diffractometer. **Optical rotations** were detected on RUDOLPH A21202-J APTV/GW.

2. Experimental procedures:

2.1 General procedure for Swern oxidation (GP I):

To a flame-dried two-neck round bottom flask, oxalyl chloride (1.5 eq) was dissolved in dry DCM (2M), and the mixture was cooled to -78 °C. DMSO (3.0 eq) was then added slowly to the reaction mixture and stirred for 15 min. afterward, alcohol (1eq) was added to the reaction mixture in DCM (0.5M), and the reaction was stirred at the same temperature for another 40 min. Finally, triethylamine (6.0 eq) was added to the reaction solution, and the reaction mixture was allowed to warm at room temperature. Afterward, the reaction solution was stirred at room temperature for 30 min, then it was quenched with water and extracted with DCM. The organic layer was washed with sodium bicarbonate and brine. The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude aldehyde was then used for the next reaction without further purification or sometimes the aldehyde can be purified by flash column chromatography.

2.2 General procedure for one carbon Wittig olefination (GP II):

To a stirred solution of methyltriphenylphosphonium iodide (1.5 eq) in THF (2M) at 0 °C was slowly added LHMDS (1.2 eq, 1 M in THF). After stirring for 30 min, the reaction mixture was cooled to 0 °C and a solution of the aldehyde (1.0 eq) in THF (2M) was added dropwise and the mixture was allowed to warm to room temperature and was stirred for 30 min. The reaction was quenched with addition of NH_4Cl and extracted with Et_2O. The combined organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude residue was purified by flash silica gel column chromatography to provide the required olefin.

2.3 General procedure for Johnson orthoester Claisen rearrangement (GP III):

The alylic alcohol (1.0 eq) was heated with $MeC(OEt)_3$ (7.0 eq) with a few drops of propionic acid for 5h, in a sealed tube. After cooling to room temperature, $MeC(OEt)_3$ was roughly distilled off under ambient pressure (bath temp: 170 ºC) and the residue was purified by silica-gel column chromatography to afford the corresponding ester.

2.4 General procedure for LAH reduction (GP IV):

$LiAlH_4$ (2.0 eq) was suspended in anhydrous ether (2M), and the suspension was cooled to 0°C. A solution of ester in dry ether (2M) was added dropwise. The reaction mixture was allowed to attain rt for 2h, and after cooling to 0 °C, it was quenched with saturated Na_2SO_4 solution carefully. It was then filtered on a celite pad, and the solid cake was washed twice with Et_2O. The combined organic layers were dried withNa_2SO_4, concentrated under reduced pressure, and purified by column chromatography to furnish the corresponding alcohol.

2.5 General procedure for asymmetric aldol reaction (GP V):

(A) Non-Evans *anti*-aldol*:*** $^{i}Pr_2NEt$ (1.15 eq) was added to a cooled (0°C) solution of oxazolidone(1.0 eq) and $(^{n}Bu)_2BOTf$ (2.0 eq, 1M in DCM) in Et_2O (2M). After stirring for 45 min at 0°C, the yellow suspension was cooled to -78 °C before a precooled (-78 °C) solution of freshly prepared aldehyde (1.3 eq) in Et_2O (1M) was slowly introduced. After an additional 30 min, the reaction mixture was quenched by addition of solid tartaric acid and the mixture stirred at ambient temperature for 2h. The reaction was partitioned between ether and H_2O, and the combined organic layers were washed with saturated aqueous $NaHCO_3$. A mixture of MeOH:30% H_2O_2 (3:1) was added under vigorous stirring at 0°C and the resulting

mixture stirred for 1h at room temperature before it was extracted with Et_2O. The combined extracts were washed with $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated. The crude material was purified by flash chromatography to afford the desired compound.

(B) Evans *syn*-aldol: $^{n}Bu_2BOTf$ (1M in CH_2Cl_2, 1.2 eq) was slowly added to a solution of oxazolidone (1.0 eq) in CH_2Cl_2 (2M) at 0 °C. Et_3N (1.3 eq) was then added at such a rate as to keep the internal temperature 0 °C. Once the addition was complete, the mixture was cooled to -78 °C before freshly prepared aldehyde (1.12 eq) was introduced. The mixture was then stirred for 30 min at –78°C. Stirring was continued for 1 h and the reaction quenched with aqueous phosphate buffer (pH 7.0) and MeOH (T < -6 °C). Next, a 1:2 mixtures of MeOH and 30% aqueous H_2O_2 was carefully added such that the internal temperature was never reached above 10 °C. The mixture was stirred for 1h once the addition was complete. After concentration on a rotary evaporator (bath-temperature ca. 30 °C), Et_2O (5mL) was added to the slurry and the aqueous phase extracted with Et_2O. The combined extracts were washed with aq. sat. $NaHCO_3$ and brine before being dried over Na_2SO_4. Evaporation of the solvent and the title compound was purified by flash chromatography.

2.6 General procedure for reductive cleavage of auxiliary (GP VI):

Method (A): $LiBH_4$ (2.4 eq) was added portion wise to a cooled (-20 °C) solution of a known aldol product (1.0 eq) and ethanol (2.4 eq) in anhydrous diethyl ether (8M) under N_2 atmosphere. The reaction mixture was stirred for 4h at -20 °C before being quenched with a saturated $NaHCO_3$ solution and extracted with Et_2O. The combined organic extracts were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The product was purified by flash chromatography to provide the desired alcohol.

Method (B): $NaBH_4$ (10.0 eq) was added to a cooled (0 °C) solution of aldol product (1.0 eq) in THF: H_2O (50 mL). The reaction mixture was then stirred for 1h at 0 °C before being quenched with water and extracted with Et_2O. The combined organic extracts were washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The product was purified by flash chromatography to yield corresponding alcohol.

2.7 General procedure for TBS-group protection (GP VII):

To a solution of alcohol (1.0 eq) in dry DMF (2M), imidazole (3.0 eq) was added at 0 °C and stirred for 10 min. TBS-Cl (2.0 eq) was then added to the reaction mixture at the same temperature, and the reaction solution was allowed to warm at room temperature and stirred for a further 1h. After completion of the reaction, the mixture was quenched with water and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solution was then concentrated under reduced pressure, and the residue was purified through flash column chromatography to furnish TBS-protected compound.

2.8 General procedure for PMB-group deprotection (GP VIII):

To a solution of compound (1.0 eq) in DCM:phosphate buffer (19:1), DDQ (1.5 eq) was added at 0 °C. The reaction mixture was then stirred for 1h at the same temperature. After completion of the reaction, the mixture was filtered through celite pad and washed with DCM. The filtrate was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The product was purified by flash column chromatography to provide compound alcohol.

2.9 General procedure for TBS-group deprotection (GP IX):
Compound (1.0 eq) was dissolved in dry DCM:MeOH (1:1, 10M) and stirred at -40 °C. CSA (0.5 eq) was then added to the reaction mixture, and the mixture was stirred at -40 °C for another 24h. The reaction solution was then quenched with water, and then extracted with DCM. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was then purified by flash column chromatography to afford the alcohol.

2.10 General procedure for DMP oxidation (GP X):
To the solution of compound (1.0 eq) in DCM (5M) at 0 °C was added $NaHCO_3$ (5.0 eq), Dess–Martin periodinane (1.2 eq) and the reaction mixture was stirred at room temperature for 1h, then saturated aqueous $Na_2S_2O_3$ solution was added and the resultant mixture was stirred at room temperature for 5 min. The mixture was extracted with DCM and the combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated. The crude aldehyde and ketone was then purified by column chromatography.

2.11 General procedure for Takai olefination (GP XI):
A solution of CHI_3 (3.2 eq) and required aldehyde (1.0 eq) in THF (9M) was added dropwise to a 0 °C suspension of $CrCl_2$ (5.0 eq) in THF (9M). The resulting mixture was stirred at room temperature for 2h before the reaction was quenched with water. The aqueous layer was extracted with ether, the combined organic phases were dried over $MgSO_4$ and evaporated, and the residue purified by flash chromatography to give (*E*)-vinylic iodide compound.

2.12 General procedure for intramolecular NHK reaction (GP XII):
The NHK reaction was carried out under argon atmosphere. To a stirred solution of $NiCl_2$ (0.1 eq) and $CrCl_2$ (7.5 eq) in degassed DMSO was added a solution of aldehyde (1.0 eq) in degassed DMSO. After being stirred at rt for 3h, the mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The combined extracts were washed with saturated brine, dried and concentrated under reduced pressure. The residue was purified by column chromatography to afford the ring closed product.

2.13 General procedure for esterification of aldol product (GP XIII):
In a typical experiment to THF (4M) was added a solution of SmI_2 (0.1 N) in THF (0.05 eq) and EtOH (10.0 eq) followed by a solution of aldol product (1.0 eq) in THF (2M). The reaction mixture was turned from blue to light yellow within a few minutes. The reaction was then monitored by TLC, which indicated total conversion of the starting product after 2h. The reaction solution was then hydrolyzed with H_2O, extracted by CH_2Cl_2, and dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel to afford the desired ester.

2.14 General procedure for methylation of –OH group (GP XIV):
Method with NaH: The alcohol (1.0 eq) was dissolved in DMF, added to reaction mixture at –40°C, with NaH (5.0 eq) in DMF and stirred for 30 min. Subsequently, MeI (5.0 eq) was then added dropwise and the reaction mixture was stirred for 4h. Then water was added and the aqueous phase was extracted with Et_2O. The combined organic phases were dried over Na_2SO_4, filtered, the solvent was removed under vacuum and the crude product was purified by column chromatography to obtain the methyl ether as a colorless oil.

Method with Ag_2O: The alcohol (1.0 eq) was dissolved in Et_2O, added to reaction mixture at room temperature, with Ag_2O (5.0 eq) in ether and stirred for 30 min. Subsequently, MeI (5.0 eq) was then added dropwise and the reaction mixture was stirred for 4h. Then water was added and the aqueous phase was extracted with Et_2O. The combined organic phases were dried over Na_2SO_4, filtered, the solvent was removed under vacuum and the crude product was purified by column chromatography to obtain the methyl ether as a colorless oil.

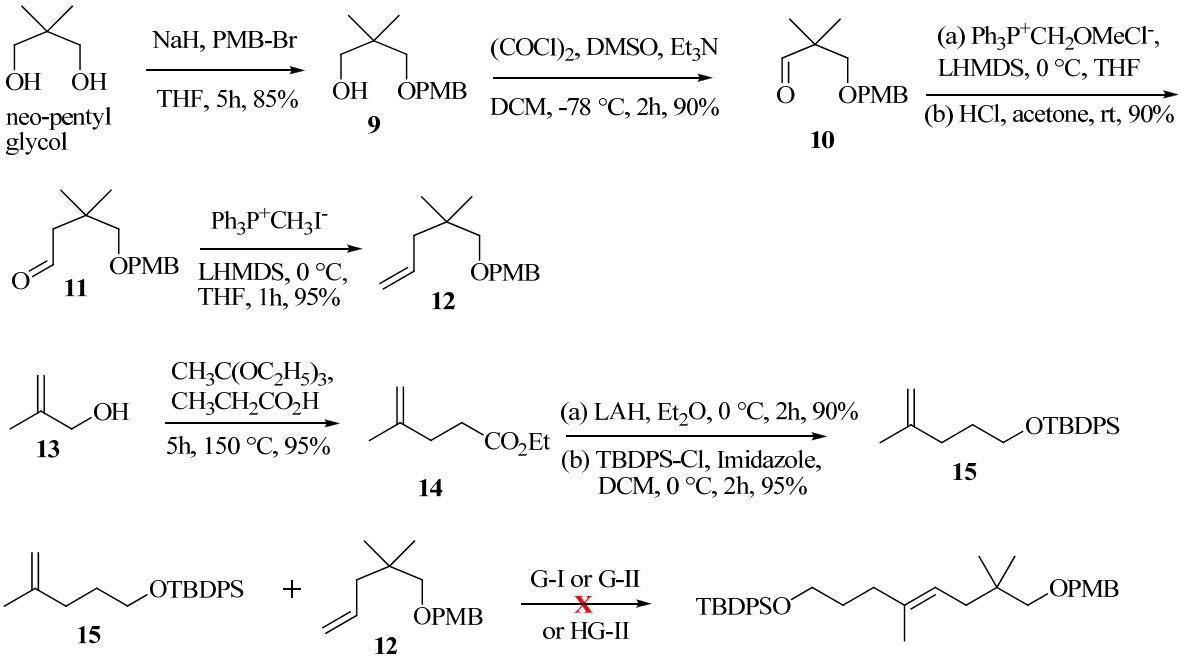
2.15 General procedure for DIBAL-H reduction (GP XV):

A 50 mL round bottom flask was charged with ester (1.0 eq), DCM and cooled to –20 °C. DIBAL-H (2.0 eq) was added to the flask. The solution was stirred for 4h and then quenched with a saturated Na/K tartrate solution. Stirring was continued until the layers became clear, followed by filtration with celite pad with DCM. The combined organic extracts filtered through a sodium sulfate plug, which was subsequently concentrated. Flash chromatography afforded the pure alcohol.

2.16 General procedure for TBDPS-group deprotection (GP XVI):

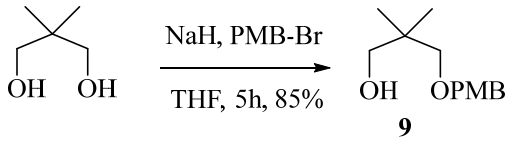
A buffered solution was prepared by addition of glacial acetic acid (12µl, 1.0 eq) to a solution of TBAF (0.4 mL, 2.0 eq). Then a stirred solution of starting (100 mg, 0.198 mmol) in THF (30 mL) was treated with the previously prepared buffer solution at 0 °C and stirred at 20°C for 6h. Then water was added and the aqueous phase was extracted with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered, Solvent was removed in vacuum and the crude product was directly applied to silica gel column chromatography and it was purified to give (+)-alashanoid E and F.

3. Synthesis of cross metathesis (CM) precursors 9 and 5:



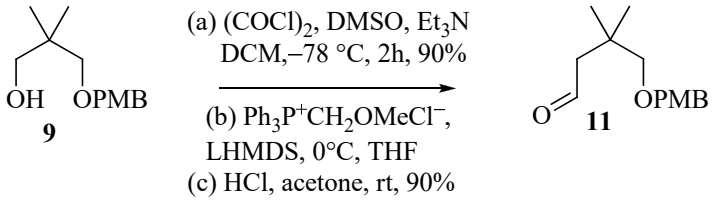
Scheme S1: Synthesis of CM precursors.

3.1: Synthesis of compound 9:



To a suspension of NaH (60%, 1.8 g, 43.2 mmol) in dry THF (70 mL), neo-pentyl glycol (48 mmol, 5 g) in dry THF (30 mL) was added dropwise at 0 °C. The solution was stirred at this temperature for 30 min. Freshly prepared PMB-Br (9.7 g, 48 mmol) in dry THF (20 mL) was then added to the reaction mixture. The reaction mixture was allowed to increase to the room temperature for 5h, and the reaction solution was quenched with saturated NH_4Cl solution (20 mL). The organic layer was separated, and the aqueous phase was washed with ethyl acetate (100 × 2 mL). The combined organic layer was washed with brine (20 mL) and dried over anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure, and the crude residue was purified by flash column chromatography to furnish compound **9** (40.12 mmol, 9.0 g, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.43 (s, 2H), 3.29 (s, 2H), 0.91 (s, 6H). **^{13}C NMR{^{1}H}** (100 MHz, $CDCl_3$) δ 159.2, 130.2, 129.1, 113.8, 79.2, 73.2, 71.8, 55.3, 36.2, 21.9. **HRMS (ESI) m/z**: for $C_{13}H_{20}O_3Na$ $[M + Na]^+$, calculated: 247.1310; found: 247.1301.

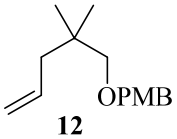
3.2: Synthesis of compound 11:



Aldehyde **10**(36.4 mmol, 8.1g, 90% yield) was synthesized by **GPI :^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 4.36 (s, 2H), 3.73 (s, 3H), 3.34 (s, 2H), 1.00 (s, 6H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 205.4, 159.2, 130.1, 129.1, 113.8, 74.7, 73.0, 55.3, 47.1, 19.1.

A round-bottom flask was charged with methoxymethyltriphenylphosphonium chloride (18 g, 57.4 mmol), and 70 ml THF was added to the flask. The solution of methoxymethyltriphenylphosphonium chloride in THF was cooled to 0 °C and the solution of potassium *tert*-butoxide (6.4 g, 57.4 mmol)in THF was added dropwise over 10 min. The mixture was stirred at 0 °C for 30 min, at which point a solution of crude aldehyde **10** (36.4 mmol, 8.1 g) in THF (20 mL) was added dropwise. The reaction was stirred at 0 °C for 15 min, the reaction was quenched with a solution of saturated aqueous NH_4Cl solution. The resulting mixture was poured water (100 mL) and diluted with EtOAc (100 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 100 mL). The organic layers were combined, dried over $MgSO_4$, and evaporated under reduced pressure. The resulting residue was hydrolyzed by 0.1N HCl then purified via flash chromatography to afford **11** (32.8 mmol, 7.8 g, 90% yield over two steps).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 4.42 (s, 2H), 3.80 (s, 3H), 3.20 (s, 2H), 2.32 (d, *J* = 1.5 Hz, 2H), 1.06 (s, 6H).**^{13}C NMR{^{1}H}** (100 MHz, $CDCl_3$) δ 203.2, 159.1, 130.5, 129.1, 113.8, 78.6, 72.9, 55.3, 53.1, 35.2, 25.2.

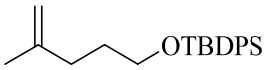
3.3: Synthesis of compound 12:



12

Compound **12** (31.16 mmol, 7.3g, 95% yield) was synthesized from **11** (32.8 mmol, 7.8g) by employing the general method as described earlier (**GPII**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 5.82-5.73(m,1H), 4.94 (d, *J* = 7.6. Hz, 2H),4.42 (s, 2H), 3.81 (s, 3H), 3.10 (s, 2H), 2.04 (d, *J* = 1.5 Hz, 2H), 0.89 (s, 6H). ^{13}C NMR**{^{1}H}** (100 MHz, $CDCl_3$) δ 159.0, 135.5, 131.1, 128.9, 116.9, 113.7, 78.7, 72.9, 55.3, 43.7, 34.9, 14.5. **HRMS (ESI) m/z**: for $C_{15}H_{23}O_2$[M + H]$^+$, calculated: 235.1698; found: 235.1692.

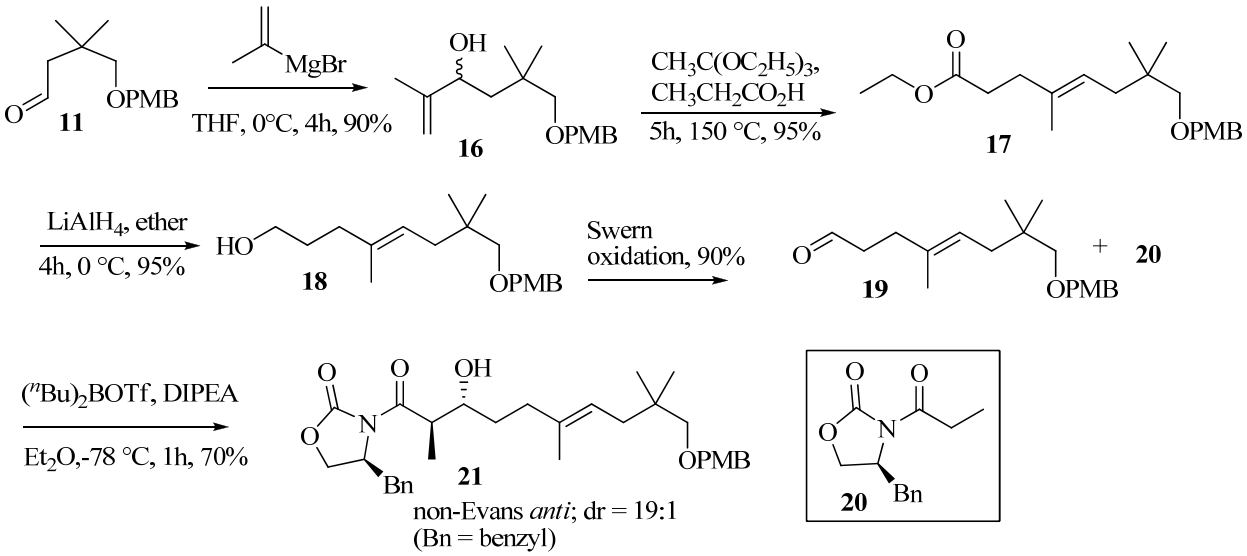
3.4: Synthesis of compound 15:



15

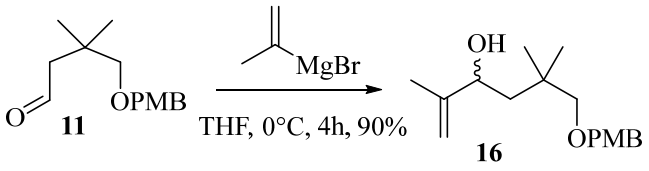
The title compound **15** (11.2 mmol, 3.8g, 81% yield over 3 steps) was synthesized from β-methallyl alcohol **13** (13.86 mmol, 1g) by employing the general method as described earlier (**GPIII**, **GPIV**) followed by TBDPS-group protection of the free hydroxyl functionality. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.6 Hz, 4H), 7.44 – 7.35 (m, 6H), 4.67 (d, *J* = 11.2 Hz, 2H), 3.67 (t, *J* = 6.4 Hz, 2H), 2.11 – 2.07 (m, 2H), 1.73 – 1.66 (overlap, 6H), 1.05 (s, 9H). **^{13}C NMR{^{1}H}** (100 MHz, $CDCl_3$) δ 145.7, 135.6, 134.1, 129.5, 127.6, 109.8, 63.6, 34.0, 30.7, 26.9, 22.5, 19.2. **HRMS (ESI) m/z**: for $C_{22}H_{31}OSi$ [M + H]$^+$, calculated: 339.2144; found: 339.2140.

4. Synthesis of aldol product 21:



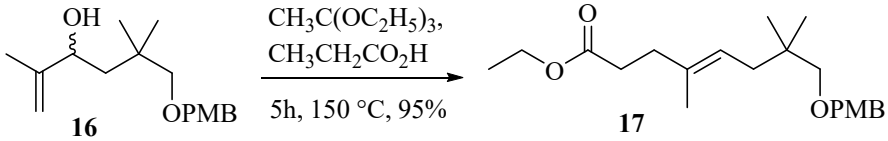
Scheme S2: Synthesis of Compound **21**.

4.1: Synthesis of compound 16:



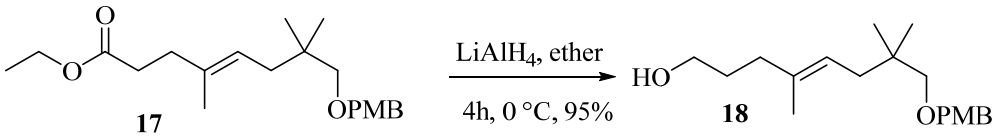
Magnesium turnings (2.0 eq, 1.9 g) was placed in a flask equipped with reflux condenser under nitrogen and small amount I_2 was added. Upon adding dibromoethane (50 µL) and THF (75 mL, 2.0M), isopropenyl bromide (1.5eq, 5.1 mL) was added dropwise while keeping the reaction mixture close to refluxing, then further stirred at 70°C for 1h. After cooling down to rt, the resulting Grignard reagent (2.0M in THF, 1.5 eq) was added to the solution of **11** (7.8 g, 32.8 mmol) at 0°C then the mixture was stirred at room temperature for 3h. The resulting reaction mixture was diluted by ethyl ether and carefully filtered through a pad silica gel. The solution was neutralized by adding NH_4Cl aqueous solution. The organic layer was then washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The compound was purified by column chromatography on silica gel to provide the desired product **16** (29.5 mmol, 8.2 g, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.96 (s, 1H), 4.76 (s, 1H), 4.47 (d, *J* = 3.7 Hz, 2H), 4.13 (d, *J* = 9.0 Hz, 1H), 3.80 (s, 3H), 3.25 (s, 2H), 1.72 (s, 3H), 1.60-1.54 (m, 1H), 1.50-1.46 (m, 1H), 1.00 (s, 3H), 0.92 (s, 3H).**^{13}C NMR{^{1}H}** (100 MHz, $CDCl_3$) δ 159.3, 148.6, 129.7, 129.4, 113.9, 109.6, 79.0, 73.2, 72.1, 55.2, 47.6, 34.3, 27.9, 23.8, 18.2. **IR**:3415,2952,2927, 2855,1611,1514,1247,1088,1036,897,820 cm^{-1}. **HRMS (ESI) m/z**: for $C_{17}H_{27}O_3$ $[M + H]^+$, calculated: 279.1960; found: 279.1936.

4.2: Synthesis of compound 17:



The obtained compound **17** (28 mmol, 9.8g, 95% yield) was synthesized from **16** (29.5 mmol, 8.2g) by employing the general method as described earlier (**GPIII**). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.4 Hz, 2H), 6.87 (d, *J* = 7.2 Hz, 2H), 5.19 (t, *J* = 7.7 Hz, 1H), 4.42 (s, 2H), 4.14 – 4.08 (m, 2H), 3.80 (d, *J* = 1.4 Hz, 3H), 3.07 (d, *J* = 1.4 Hz, 2H), 2.42 – 2.37 (m, 2H), 2.33 – 2.29 (m, 2H), 1.96 (d, *J* = 7.7 Hz, 2H), 1.60 (s, 3H), 1.27 – 1.23 (m, 3H), 0.86 (s, 6H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 173.4, 158.9, 134.9, 131.2, 128.9, 121.8, 113.7, 78.6, 72.9, 60.2, 55.2, 37.0, 35.7, 35.0, 33.4, 24.5, 16.1, 14.2. **IR**: 2956, 2929, 2853, 1736, 1614, 1513, 1464, 1374, 1299, 1244, 1172, 1094, 1037, 822 cm^{-1}. **HRMS (ESI) m/z**: for $C_{21}H_{33}O_4$ $[M + H]^+$, calculated: 349.2379; found: 349.2359.

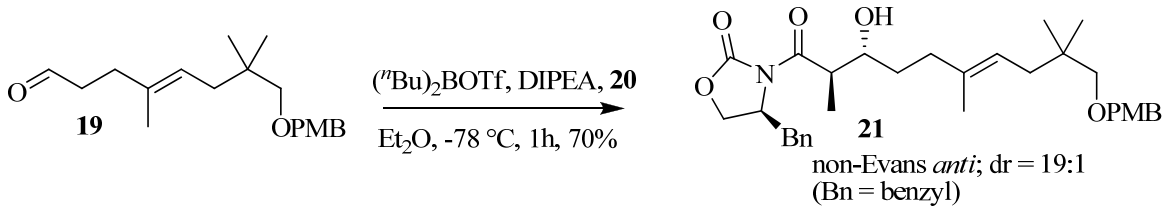
4.3: Synthesis of compound 18:



Compound **18** (26.63 mmol, 8.2g, 95% yield) was synthesized from **17** (28 mmol, 9.8g) by employing the general method as described earlier (**GPIV**). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 6.3 Hz, 2H), 6.88

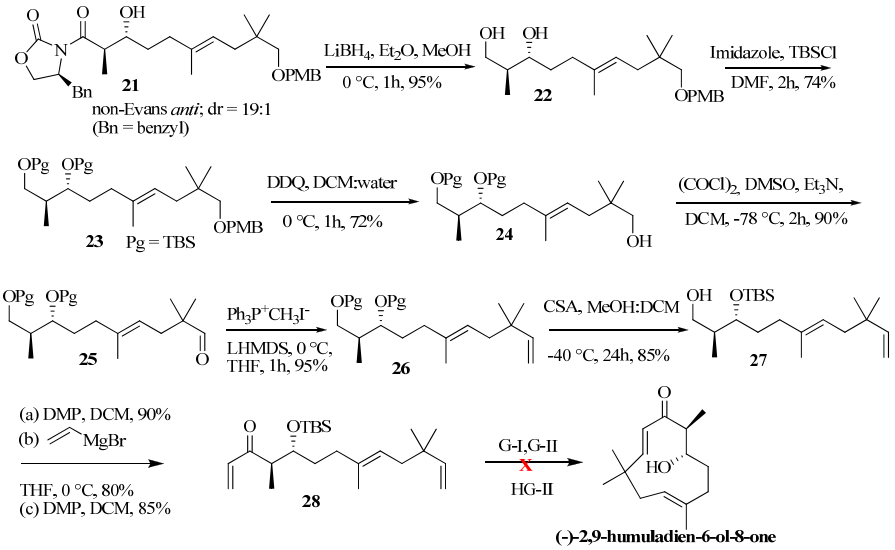
(d, J = 8.6 Hz, 2H), 5.18 (t, J =7.7 Hz, 1H), 4.43 (s, 2H), 3.81 (s, 3H), 3.62 (t, J = 6.5 Hz, 2H), 3.08 (s, 2H), 2.06 (t, J = 7.5 Hz, 2H), 1.97 (d, J = 7.7 Hz, 2H), 1.69-1.62 (m, 2H), 1.60 (s, 3H), 1.47 (s, 1H), 0.87 (s, 6H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 158.9, 136.2, 131.2, 128.9, 121.4, 113.7, 78.6, 72.9, 62.8, 55.3, 37.2, 36.3, 35.7, 30.9, 24.6, 16.0. **IR:** 3372, 2926, 2850, 1514, 1247, 1172, 1092, 1037, 821 cm^{-1}. **HRMS (ESI) m/z**: for $C_{19}H_{31}O_3$ $[M + H]^+$, calculated: 307.2273; found: 307.2253.

4.4: Synthesis of compound 21:



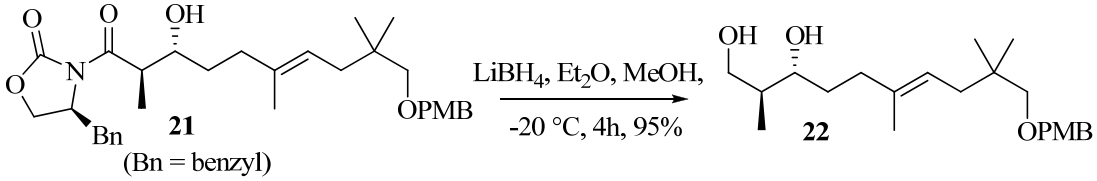
Synthesis of aldehyde **19** (23.97 mmol, 7.3g, 90% yield) from **18** (26.63 mmol, 8.2g) was done by employing the general method as described earlier (**GP1)**. Synthesis of compound **21** (16.73 mmol, 9g, 70% yield) was achieved by using aldehyde **19** (23.97 mmol, 7.3g) and auxiliary **20** (18.4 mmol, 4.3g) followed by non-Evans *anti* aldol method (**GPVA**). $[\alpha]_D^{25}$= +12.7(c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 (d, J = 7.4 Hz, 2H), 7.16 – 7.10 (m, 5H), 6.75 (d, J = 8.5 Hz, 2H), 5.12 (t, J = 7.5 Hz, 1H), 4.59 – 4.55 (m, 1H), 4.30 (s, 2H), 4.09 – 4.03 (m, 2H), 3.82 – 3.80 (m, 1H), 3.68 (s, 3H), 3.62 (t, J = 6.4 Hz, 1H), 3.23-3.19 (m, 1H), 2.98 (s, 2H), 2.66-2.61 (m, 1H), 2.16 – 2.10 (m, 1H), 2.03 – 1.97 (m, 1H), 1.86 (d, J = 7.7 Hz, 2H), 1.65-1.58 (m,1H), 1.49 (s, 3H), 1.47 – 1.42 (m, 1H), 1.10 (d, J = 6.8 Hz, 3H), 0.76 (s, 6H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 176.8, 158.9, 153.5, 136.1, 135.3, 131.2, 129.4, 128.9, 128.9, 127.3, 121.6, 113.7, 78.8, 74.4, 72.9, 66.0, 55.5, 55.3, 43.2, 37.9, 37.2, 35.9, 35.7, 33.4, 24.6,16.2, 14.6. **IR:** 3528, 2954, 2924, 2854, 1780, 1697, 1613, 1513, 1455, 1382, 1247, 1210, 1097, 1033, 822, 763,7 50, 703, 507cm^{-1}. **HRMS (ESI) m/z**: for $C_{32}H_{44}NO_6$ $[M + H]^+$, calculated: 538.3169; found: 538.3168.

5. Synthesis of RCM precursor 28:



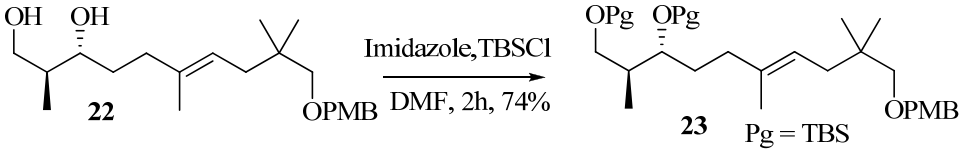
Scheme S3: Synthesis of Compound **28**.

5.1: Synthesis of compound 22:



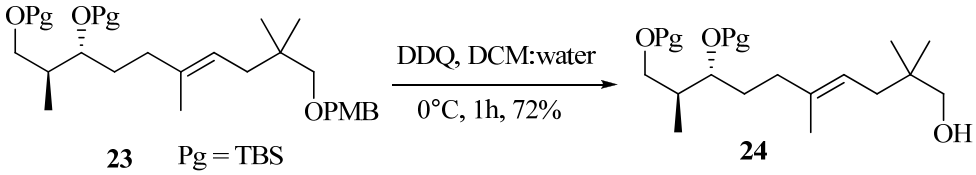
Compound **22** (15.9 mmol, 5.8 g, 95% yield) was synthesized from **21** (16.73 mmol, 9g) by employing the general method as described earlier **(GPVIA)**. $[\alpha]_D^{25}$= -29.7(c = 0.1,MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.19 (t, *J* = 7.5 Hz, 1H), 4.41 (s, 2H), 3.78 (s, 4H), 3.67 (d, *J* = 5.4 Hz, 2H), 3.07 (s, 2H), 2.24-2.20 ((broad peak for 2 OH and marked H), 3H), 2.17 – 2.11 (m, 1H), 2.06 – 2.00 (m, 1H), 1.96 (d, *J* = 7.7 Hz, 2H), 1.79-1.75 (m, 1H), 1.59 (s, 3H), 1.53-1.46 (m, 1H), 0.90 (d, *J* = 7.1 Hz, 3H), 0.86 (s, 6H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 159.0, 136.4, 131.2, 128.9, 121.6, 113.7, 78.7, 74.4, 72.9, 67.2, 55.3, 39.2, 37.2, 36.8, 35.7, 32.2, 24.6, 24.6, 16.1, 10.2. **IR**: 3673, 3415, 2924, 2756, 2658, 1624, 1530, 1467, 1340, 1188, 1010, 890, 735, 620, 507 cm^{-1}. **HRMS (ESI) m/z**: for $C_{22}H_{37}O_4$ $[M + H]^+$, calculated: 365.2692; found: 365.2693.

5.2: Synthesis of compound 23:



Compound **23** (11.8 mmol, 7g, 74% yield) was furnished from **22** (15.9 mmol, 5.8g) by employing the general method as described earlier (**GPVII**). $[\alpha]_D^{25}$= -11.0 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 6.9 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.14 (t, *J* = 7.5 Hz, 1H), 4.39 (s, 2H), 3.77 (s, 3H), 3.67-3.64 (m, 1H), 3.57-3.54 (m, 1H), 3.41-3.38 (m, 1H), 3.06 (s, 2H), 2.07-2.01 (m, 1H), 1.93 (d, *J* = 7.7 Hz, 3H), 1.82 – 1.77 (m, 1H), 1.55 (s, 3H), 1.48-1.43 (m, 2H), 0.86-0.81 (m, 27H), -0.00 (s, 12H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 158.9, 137.2, 131.3, 128.8, 120.6, 113.7, 78.9, 73.2, 72.9, 65.2, 55.2, 40.8, 37.1, 35.7, 31.7, 25.9, 24.5, 18.3, 18.1, 16.2, 12.4, -4.3, -4.5, -5.3, -5.4. **IR**:2954,2928,2856,1614,1514,1472,1360,1248,1088,1040,834,774,666cm^{-1}. **HRMS (ESI) m/z**: for $C_{34}H_{65}O_4Si_2$ $[M + H]^+$, calculated: 593.4421; found: 593.4428.

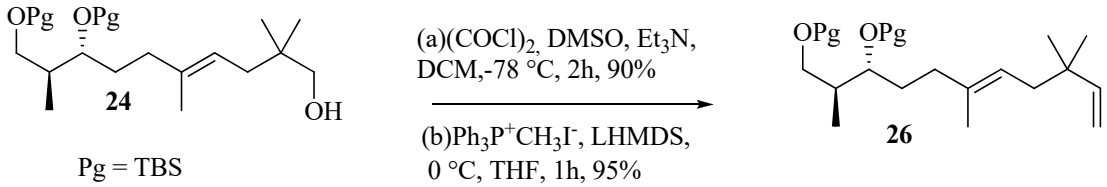
5.3: Synthesis of compound 24:



Title compound **24** (8.5 mmol, 4g, 72% yield) was synthesized from **23** (11.8 mmol, 7g) by employing the general method as described earlier (**GPVIII**). $[\alpha]_D^{25}$= -25.2 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.18 (t, *J* = 7.2 Hz, 1H), 3.68-3.65 (m, 1H), 3.56 – 3.52 (m, 1H), 3.41-3.38 (m, 1H), 3.29 (s, 2H), 2.09 – 2.03 (m, 1H), 1.99-1.94 (m, 1H), 1.92 (d, *J* = 7.8 Hz, 2H), 1.81-1.77 (m, 1H), 1.58 (s, 3H), 1.49 – 1.44 (m, 2H), 0.86 – 0.80 (m, 27H), -0.00 (s, 12H).**^{13}C NMR {^{1}H}** (125 MHz, $CDCl_3$) δ 137.6, 120.2, 73.1, 71.9, 65.2, 40.8, 36.8, 36.2, 35.7, 31.5, 25.9, 23.8, 18.2, 18.1, 16.2, 12.2, -4.3, -4.5, -5.3, -5.4.

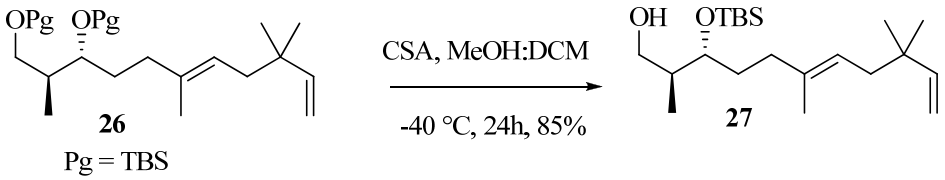
IR: 3442, 2944, 2924,2 856, 1756, 1492, 1322, 1226, 1022, 816, 630 cm^{-1}. **HRMS (ESI) m/z**: for $C_{26}H_{57}O_3Si_2$ $[M + H]^+$, calculated: 473.3846; found: 473.3840.

5.4: Synthesis of compound 26:



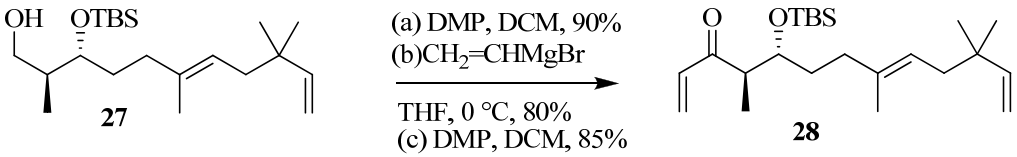
Compound **26** (7.2 mmol, 3.4g, 85% yield over 2 steps) was synthesized from **24** (8.5 mmol, 4g) by employing the general method as described earlier (**GPI** and **GPII**). $[\alpha]_D^{25}$= -32.3 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.77 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.11 (t, *J* = 7.4 Hz, 1H), 4.88 – 4.85 (m, 2H), 3.66 (dd, *J* = 10.6, 5.3 Hz, 1H), 3.55 (dd, *J* = 9.8, 6.3 Hz, 1H), 3.39 (dd, *J* = 9.9, 6.7 Hz, 1H), 2.07 – 2.01 (m, 1H), 1.98-1.93 (overlap, 3H), 1.81 – 1.76 (m, 1H), 1.55 (s, 3H), 1.49 – 1.43 (m, 2H), 0.94 (s, 6H), 0.86 (s, 18H), 0.81 (d, *J* = 6.9 Hz, 3H), -0.00 (s, 12H). **^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 148.6, 137.0, 120.8, 110.0, 73.1, 65.2, 40.8, 40.5, 37.4, 35.6, 31.6, 26.5, 26.5, 25.9, 18.3, 18.2, 16.3, 12.4, -4.3, -4.5, -5.4, -5.5. **IR**: 2904, 2874, 2846, 1706, 1462, 1320, 1212, 1011, 810, 610 cm^{-1}. **HRMS (ESI) m/z**: for $C_{27}H_{57}O_2Si_2$ $[M + H]^+$, calculated: 469.3897; found: 469.3891.

5.5: Synthesis of compound 27:



Compound **27** (6.1 mmol, 2.1g, 85% yield) was synthesized from **26** (7.2 mmol, 3.4g) by employing the general method as described earlier (**GPIX**). $[\alpha]_D^{25}$= -68.3 (c = 0.1, MeOH). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 – 5.68 (m, 1H), 5.05 (t, *J* = 5.3 Hz, 1H), 4.81 (dd, *J* = 14.4, 3.4 Hz, 2H), 3.72-3.65 (m, 1H), 3.62–3.58 (m, 1H), 3.47 – 3.41 (m, 1H), 2.03 – 1.81 (m, 4H), 1.72 – 1.64 (m, 1H), 1.58 (dd, *J* = 14.0, 8.0 Hz, 1H), 1.50 (s, 3H), 0.92– 0.88 (overlap, 9H), 0.81 (s, 9H), 0.74 (d, *J* = 7.0 Hz, 1H), -0.00 (s, 6H).**^{13}CNMR{^{1}H}** (125 MHz, $CDCl_3$) δ 148.4, 136.1, 121.4, 110.1, 75.4,65.3,40.5,37.4,35.2,33.3,26.5, 26.5,25.8,17.9,16.2,14.7,11.7,-4.3,-4.7. **IR**: 3342, 2900, 2854, 2816, 1736, 1472,1300,1216,1022,720,620 cm^{-1}. **HRMS (ESI) m/z**: for $C_{21}H_{43}O_2Si$ $[M + H]^+$, calculated: 355.3032; found: 355.3029.

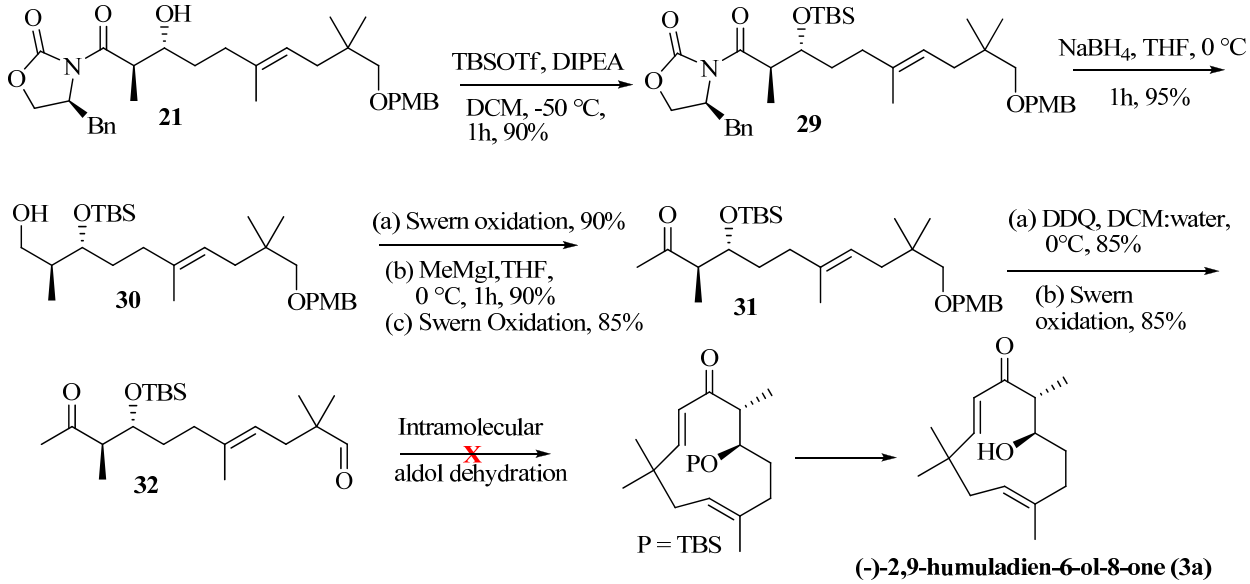
5.6: Synthesis of compound 28:



Compound **28** (3.7 mmol, 1.4g, 65% yield over 3 steps) was synthesized from **27** (6.1 mmol, 2.1g) by DMP oxidation **(GPX)**, vinyl Grignard reaction then DMP oxidation (**GPX**). $[\alpha]_D^{25}$= -43.4 (c = 0.1,

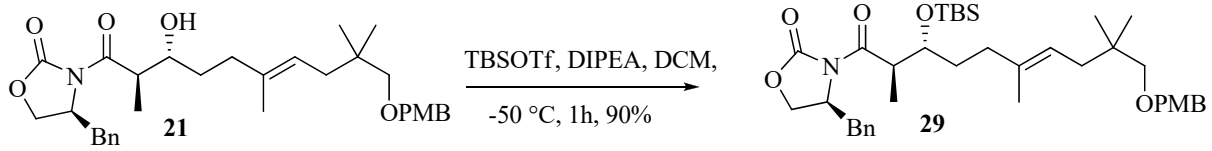
MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.46 – 6.37 (m, 1H), 6.18 (dd, *J* = 17.4, 3.1 Hz, 1H), 5.77 – 5.66 (m, 2H), 5.09 (q, *J* = 7.5 Hz, 1H), 4.86 – 4.83 (m, 2H), 3.96 – 3.91 (m, 1H), 3.04-2.98 (m, 1H), 2.08 – 1.91 (overlap, 4H), 1.52 – 1.49 (overlap, 5H), 0.97 (d, *J* = 7.0 Hz, 3H), 0.92 (s, 6H), 0.80 (s, 9H), -0.00 (s, 6H). **^{13}C NMR{^{1}H}** (126 MHz, $CDCl_3$) δ 203.33, 148.48, 136.56, 135.72, 127.71, 121.19, 110.07, 73.32, 48.24, 40.53, 37.36, 35.40, 34.03, 32.38, 26.47, 25.86, 18.05, 16.25, 12.33, 11.76, -4.42, -4.83. **IR**:2900,2844,2832,1766,1642, 1572,1420,1316,1032,850,740 cm^{-1}. **HRMS (ESI) m/z**: for $C_{23}H_{43}O_2Si$ $[M + H]^+$, calculated: 379.3032; found: 379.3031.

6. Synthesis of intramolecular aldol precursor 32:



Scheme S4: Synthesis of Compound **26**.

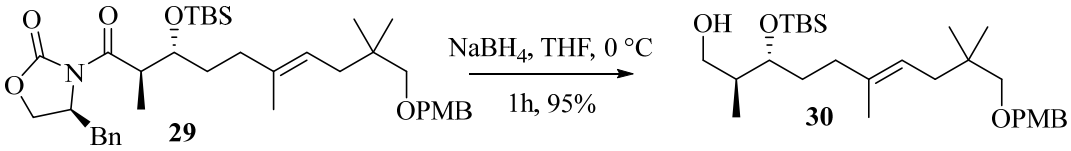
6.1: Synthesis of compound 29:



A solution of the foregoing aldol adduct **21** (16.7 mmol, 9g) in DCM (10 mL) was cooled to –50 °C. Then, DIPEA (1.7 mL, 9.4 mmol) followed by TBSOTf (1.45 mL, 6.3 mmol) were added. The reaction mixture was stirred for 1h. The mixture was treated with H_2O and extracted with DCM. The combined organic extracts were washed saturated $NaHCO_3$ and saturated NaCl solution, dried over Na_2SO_4, filtered, and concentrated in vacuo. Flash chromatography afforded TBS-protected compound **29** (15 mmol, 9.8g, 90% yield). $[\alpha]_D^{25}$= +27.0 (c = 0.1, MeOH). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 7H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.17 (t, *J* = 7.4 Hz, 1H), 4.60 (td, *J* = 7.0, 3.8 Hz, 1H), 4.42 (s, 2H), 4.27 – 4.05 (m, 2H), 4.02 (dd, *J* = 10.7, 5.4 Hz, 1H), 3.96 – 3.82 (m, 1H), 3.80 (s, 3H), 3.29 (dd, *J* = 13.3, 2.7 Hz, 1H), 3.09 (s, 2H), 2.78 (dd, *J* = 13.2, 9.7 Hz, 1H), 2.11 – 1.84 (m, 4H), 1.82 – 1.46 (m, 6H), 1.23 (d, *J* = 6.8 Hz, 3H), 0.90,0.88 (overlap, 16H), 0.03 (d, *J* = 18.5 Hz, 6H). **^{13}C NMR {^{1}H}** (100 MHz, $CDCl_3$) δ 175.3, 158.9, 153.1, 136.6, 135.4, 131.2, 129.5, 128.9, 128.8, 127.3, 120.8, 113.6, 78.8, 72.9, 72.8, 66.0, 55.8, 55.2, 42.7, 37.6, 37.1, 35.7, 35.4, 34.4, 25.8, 24.5, 18.1, 16.2, 11.7, -4.1, -4.8. **IR**: 2954, 2927, 2855, 1785,

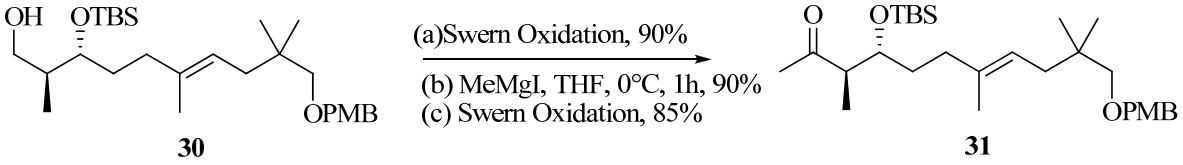
1702, 1513, 1462, 1380, 1361, 1350, 1248, 1209, 1195, 1101, 1040, 1017, 836, 775, 702 cm^{-1}. **HRMS (ESI) m/z**: for $C_{38}H_{58}NO_6Si$ $[M + H]^+$, calculated: 652.4033; found: 652.4031.

6.2: Synthesis of compound 30:



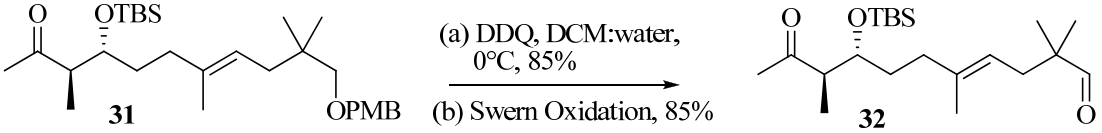
Compound **30** (14.2 mmol, 6.8g, 95% yield) was synthesized from **29** (15 mmol, 9.8g) by employing the general method as described earlier (**GPVIB**). $[\alpha]_D^{25}$= -17.8 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 5.07 (q, *J* = 7.5 Hz, 1H), 4.34 (s, 2H), 3.71 (s, 3H), 3.69 – 3.65 (m, 1H), 3.60 (dd, *J* = 14.2, 8.2 Hz, 1H), 3.47 – 3.40 (m, 1H), 3.00 (s, 2H), 2.00 – 1.80 (m, 5H), 1.70 – 1.66 (m, 1H), 1.61 – 1.55 (m, 1H), 1.50 (s, 3H), 0.92 – 0.73 (m, 18H), -0.00 (s, 6H). **^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 158.9, 136.3, 131.2, 128.8, 121.2, 113.7, 78.8, 75.4, 72.9, 65.3, 55.2, 39.5, 37.6, 37.1, 35.7, 35.3,3 3.4, 25.9, 24.6, 24.5, 18.0, 16.1, 14.7, 11.8, -4.2, -4.7. **IR**: 3344, 2934, 2918, 2816, 1624, 1564, 1478, 1310, 1278, 1018, 1000, 804, 724, 636 cm^{-1}. **HRMS (ESI) m/z**: for $C_{28}H_{51}O_4Si$ $[M + H]^+$, calculated: 479.3557; found: 479.3551.

6.3: Synthesis of compound 31:



Compound **31** (9.8 mmol, 4.8g, 68% yield over 3 steps) was prepared from **30** (14.2 mmol, 6.8g) by employing the general method as described earlier (**GPI**). $[\alpha]_D^{25}$= -12.0 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.4 Hz,2H), 6.77 (d, *J* = 8.6 Hz, 2H), 5.08 (dd, *J* = 18.9, 7.2 Hz, 1H), 4.33 (s, 2H), 3.83 (dd, *J* = 8.4, 3.4 Hz, 1H), 3.71 (s, 3H), 2.99 (s, 2H), 2.66 – 2.64 (m, 1H), 2.25 (q, *J* = 7.2 Hz, 1H), 2.06 (s, 3H), 1.90-1.86 (m, 3H), 1.48 (s, 3H), 0.92 (d, *J* = 7.0 Hz, 2H), 0.82 – 0.79 (overlap, 15H), -0.00 (s, 6H). **IR**: 2954, 2927, 2854, 1716, 1670, 1613, 1513, 1463, 1361, 1248, 1172, 1094, 1056, 1038, 836, 775 cm^{-1}. **HRMS (ESI) m/z**: for $C_{29}H_{51}O_4Si$ $[M + H]^+$, calculated: 491.3557; found: 491.3553

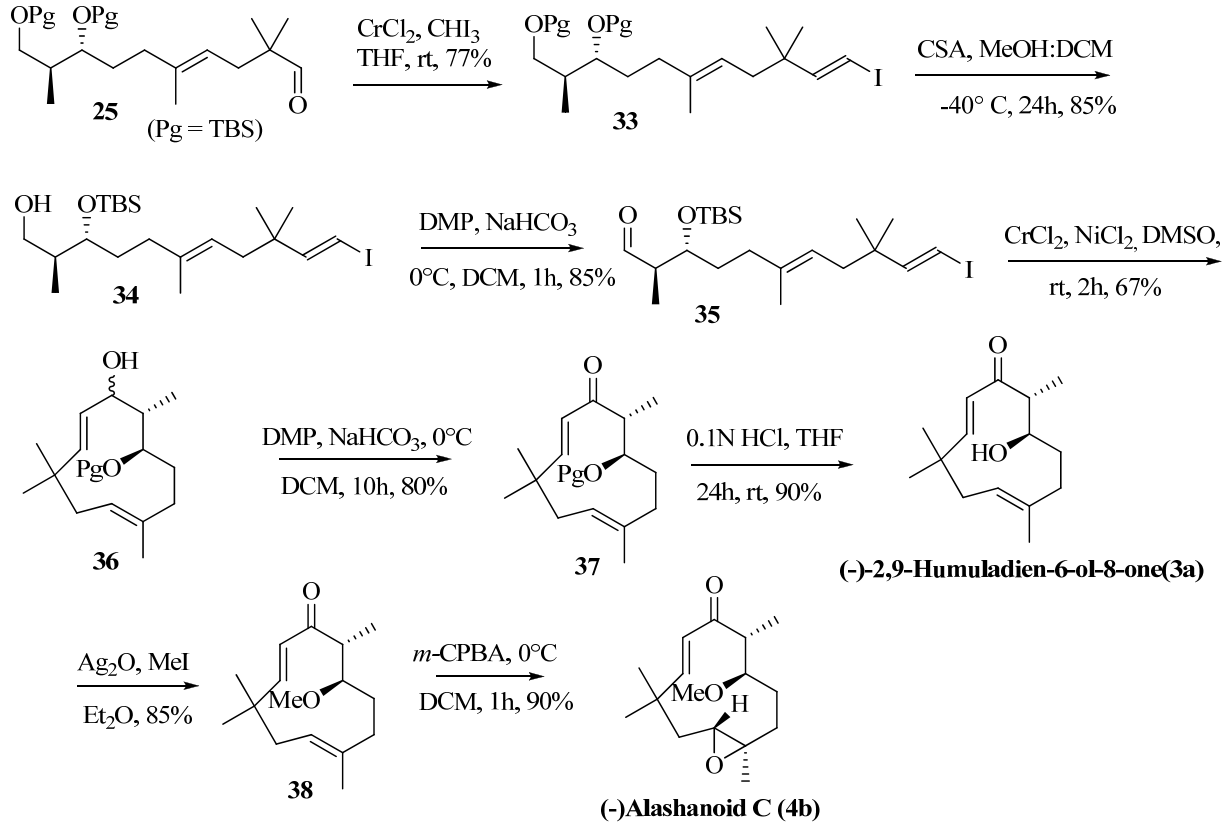
6.4: Synthesis of compound 32:



Compound **32** (7 mmol, 2.6g, 72% yield over 2 steps) was synthesized from **31** (9.8 mmol, 4.8g) by employing the general method as described earlier (**GPVIII** and **GPI**. $[\alpha]_D^{25}$= -47.9 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.41 (s, 1H), 5.02 (t, *J* = 7.5 Hz, 1H), 3.85 (dd, *J* = 10.6, 5.5 Hz, 1H), 2.68 – 2.65 (m, 1H), 2.12-2.09 (m, 5H), 2.02 – 1.86 (m, 2H), 1.53 (s, 3H), 1.50-1.43 (m, 1H), 1.42 – 1.37 (m, 1H), 0.98 (s, 6H), 0.82 (s, 9H), -0.00 (s, 6H).**^{13}CNMR {^{1}H}** (125 MHz, $CDCl_3$) δ 211.8, 206.2, 138.3,

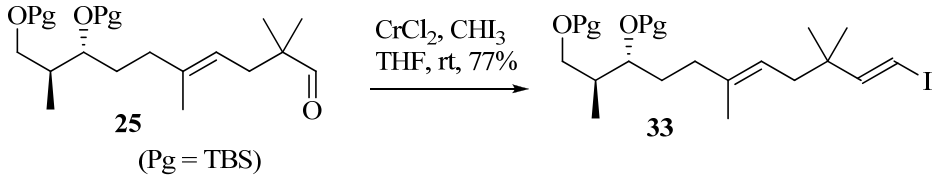
118.7, 73.4, 51.5, 46.5, 35.4, 34.2, 33.2, 32.3, 30.5, 25.8, 21.1, 18.0, 16.2, 12.3, 11.5, -4.4, -4.9. **IR**: 2950, 2927, 2851, 1616, 1600, 1573, 1513, 1463, 1369, 1221, 1112, 1014, 1006, 938, 836, 775 cm^{-1}.

7. Synthesis of (-)-2,9-humuladien-6-ol-8-one and (-)-alashanoid C (4b):



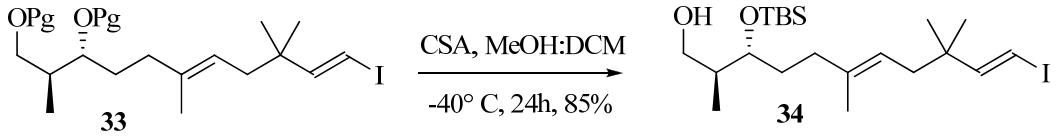
Scheme S5: Synthesis of **(-)-2,9-humuladien-6-ol-8-one** and **(-)-alashanoid C(4b).**

7.1: Synthesis of compound 33:



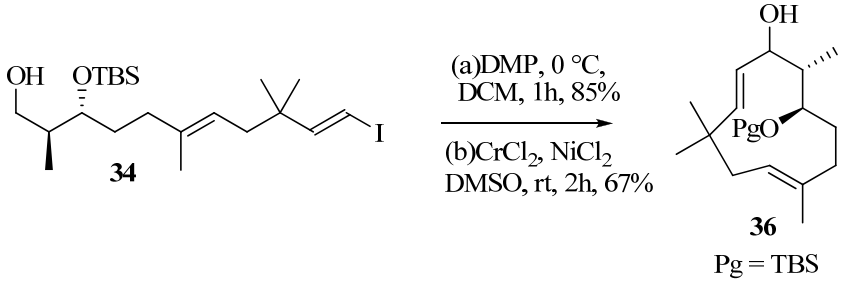
Compound **33** (5.9 mmol, 3.5g, 77% yield) was synthesized from **25** (7.6 mmol, 3.5g) by employing the general method as described earlier (**GPXI**). $[\alpha]_D^{25}$= -28.2 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.47 (d, *J* = 14.6 Hz, 1H), 5.86 (d, *J* = 14.6 Hz, 1H), 5.07 (t, *J* = 7.0 Hz, 1H), 3.68-3.65(m, 1H), 3.56-3.53 (m, 1H), 3.41 – 3.38 (m, 1H), 2.07-2.01 (m, 1H), 1.98-1.92 (m, 3H), 1.81 – 1.76 (m, 1H), 1.54 (s, 3H), 1.47 – 1.43 (m, 2H), 0.94 (s, 6H), 0.86 (s, 18H), 0.81 (d, *J* = 6.9 Hz, 3H), -0.00 (s, 12H).**^{13}CNMR{^{1}H}** (125MHz, $CDCl_3$) δ 155.7, 138.1, 119.7, 73.1, 72.2, 65.2, 41.6, 40.8, 40.2, 35.6, 26.0, 26.0,25.9,18.2,18.1,16.2,12.3,-4.2,-4.5,-5.3,-5.4. **IR**: 2930, 2907, 2770, 1756, 1424, 1312, 1126, 1022, 916, 830 cm^{-1}. **HRMS (ESI) m/z**: for $C_{27}H_{56}IO_2Si_2$ $[M + H]^+$, calculated: 595.2864; found: 595.2850.

7.2. Synthesis of compound 34:



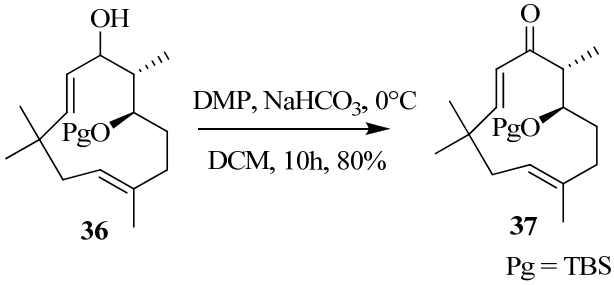
Compound **34** (5 mmol, 2.4g, 85% yield) was achieved from **33** (5.9 mmol, 3.5g) by employing the general method as described earlier (**GPIX**). $[\alpha]_D^{25}$= -62.7 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.40 (d, *J* = 14.6 Hz, 1H), 5.81 (d, *J* = 14.6 Hz, 1H), 5.01(t, *J* = 7.5 Hz, 1H), 3.70-3.67 (m, 1H), 3.62-3.58 (m, 1H), 3.48-3.44 (m, 1H),1.93 – 1.87 (m, 4H), 1.71-1.66 (m, 1H), 1.58 – 1.54 (m, 2H), 1.49 (s, 3H), 0.91 – 0.89 (m, 9H), 0.81 (s, 9H), -0.00 (s, 6H).**^{13}CNMR {^{1}H}** (125 MHz, $CDCl_3$) δ 155.6, 137.2, 120.3, 76.9, 72.3, 65.4, 41.6, 40.2, 37.9, 35.1, 33.4, 26.1, 26.0, 25.8, 18.0, 16.2, 14.5, -4.1, 4.6. **IR**: 3372, 2934,2900, 2820, 2750, 1646, 1434, 1382, 1166, 1022, 986, 810cm^{-1}. **HRMS(ESI) m/z** for $C_{21}H_{42}IO_2Si$ $[M + H]^+$, calculated: 481.1999; found: 481.1994.

7.3. Synthesis of compound 36:



Compound **34** (5 mmol, 2.4g) was reacted under condition according to **GPX** and **GPXII** to afford **36** (2.8 mmol, 1g, 57% yield over 2 steps). $[\alpha]_D^{25}$= -70.0 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.16 (d, *J* = 15.7 Hz, 1H), 5.04-5.01 (m, 1H), 4.99 – 4.96 (m, 1H), 3.65 – 3.63 (m, 1H), 3.41 (t, *J* = 9.4 Hz, 1H), 2.14 (t, *J* = 12.5 Hz, 1H), 1.89-1.85 (m, 1H), 1.79 (t, *J* = 11.9 Hz, 1H), 1.73 – 1.70 (m, 1H), 1.59 – 1.55 (m, 1H), 1.48 (s, 3H), 1.30-1.25 (m, 1H), 1.04 (s, 3H), 0.99 (s, 3H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.80 (s, 9H), -0.00 (s, 6H).**^{13}CNMR {^{1}H}** (125 MHz, $CDCl_3$) δ 143.2, 137.1, 127.2, 122.1, 77.5, 72.0, 47.2, 41.5, 38.2, 36.5, 30.0, 29.8, 25.8, 23.9, 17.9, 17.0, 9.6, 3.9, 4.0. **IR**:3456,2995,2890,2860,2723,1596,1447,1405,1246,1139,1142,1081,911,790 cm^{-1}. **HRMS (ESI) m/z**: for $C_{21}H_{41}O_2Si$ $[M + H]^+$, calculated: 353.2876; found: 353.2874.

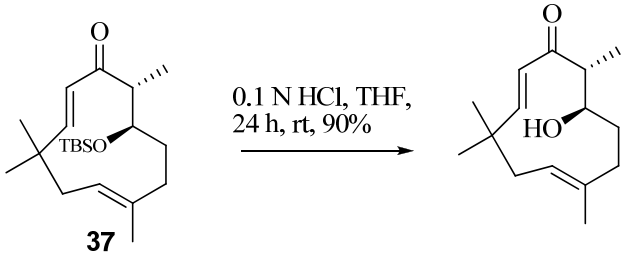
7.4. Synthesis of compound 37:



Compound **37** (0.22 mmol, 78mg, 80% yield) was synthesized from **36** (0.28 mmol, 100mg) according to **GPX**. $[\alpha]_D^{25}$= -106.0 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.00 (d, *J* = 16.1 Hz, 1H), 5.91 (d,

J = 16.1 Hz, 1H), 4.92 (dd, *J* = 11.6, 4.3 Hz, 1H), 4.06 – 4.04 (m, 1H), 2.62 – 2.57 (m, 1H), 2.09 (t, *J* = 12.4 Hz, 1H), 1.88-1.84 (m, 1H), 1.74 – 1.69 (m, 2H), 1.41 (s, 2H), 1.22 (s, 3H), 1.02 (s, 3H), 0.99 (s, 3H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.77 (s, 9H), -0.00 (s, 6H).**^{13}CNMR {^{1}H}** (125 MHz, $CDCl_3$) δ 201.1, 151.4, 138.4, 128.2, 121.5, 73.1, 55.2, 41.4, 39.9, 37.5, 30.3, 28.9, 25.7, 22.8, 17.9, 16.4, 6.0, -4.1, -4.3. **IR**: 2955, 2928, 2855, 1699, 1629, 1463, 1253, 1083, 1073, 910, 836, 773, 674cm^{-1}. **HRMS (ESI) m/z**: for $C_{21}H_{39}O_2Si$ $[M + H]^+$, calculated: 351.2719; found: 351.2723.

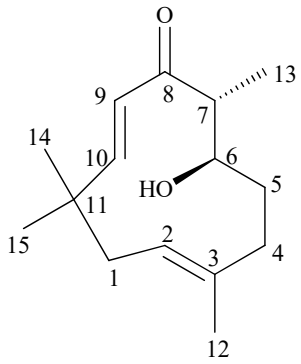
7.5: Synthesis of (-)-2,9-humuladien-6-ol-8-one (3a):

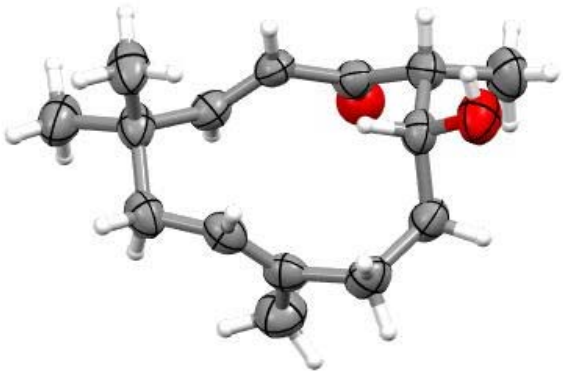


37 **(-)-2,9-Humuladien-6-ol-8-one (3a)**

To the solution of compound **37** (78mg, 0.22 mmol) in THF (15 mL) at 0 °C was added 0.1N HCl (2.5 mL) and the reaction mixture was stirred at room temperature for 24h, then water was added and the mixture was extracted with EtOAc and the combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography to afford (-)-2,9-Humuladien-6-ol-8-one **(3a)** (0.2 mmol, 47mg, 90% yield)**.** $[\alpha]_D^{25}$= -97.8 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.15 (d, *J* = 16.0 Hz, 1H), 6.10 (d, *J* = 16.0 Hz, 1H), 5.08 (dd, *J* = 11.0, 3.5 Hz, 1H), 4.22 (m, 1H), 2.90 (m, 1H), 2.21 (t, *J* = 12.0 Hz, 1H), 2.07 (dd, *J* = 12.5, 3.5 Hz, 1H), 1.95 (t, *J* = 12.0 Hz, 1H), 1.86 (dd, *J* = 13.0, 3.5 Hz, 1H), 1.37(s, 3H), 1.30(m, 1H), 1.16 (s, 3H), 1.11 (m, 1H), 1.12 (s, 3H), 1.03 (d, *J* = 6.5 Hz, 3H). **^{13}CNMR {^{1}H}** (125 MHz, $CDCl_3$) δ 201.0, 152.0, 137.8,128.1,122.2,73.0,54.3, 41.3, 40.0, 37.7, 30.7, 28.9, 23.0, 16.4, 6.1. **IR**: 3480, 2965, 2936, 2872, 2856, 1669, 1619, 1453, 1387, 1302, 1083, 1049, 1007, 999, 988 cm^{-1}.**HRMS (ESI) m/z**:for $C_{15}H_{25}O_2$ $[M + H]^+$, calculated: 237.1855;found: 237.1853.

NMR comparison data of natural and synthetic (-)-2,9-Humuladien-6-ol-8-one (3a)

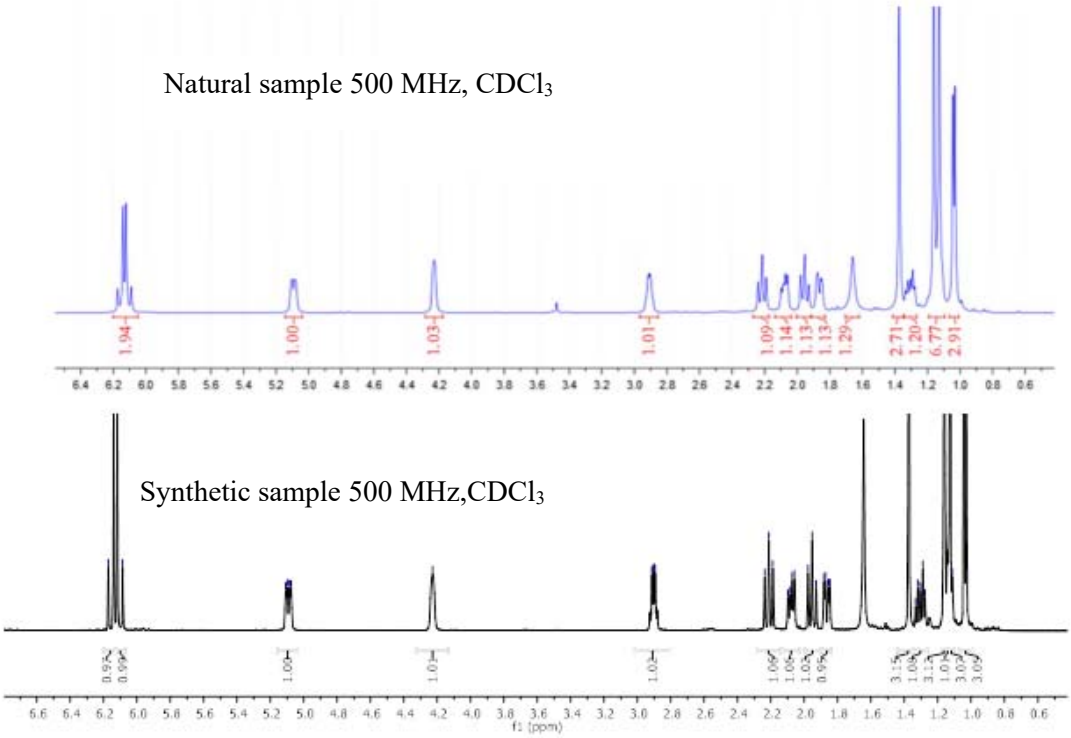




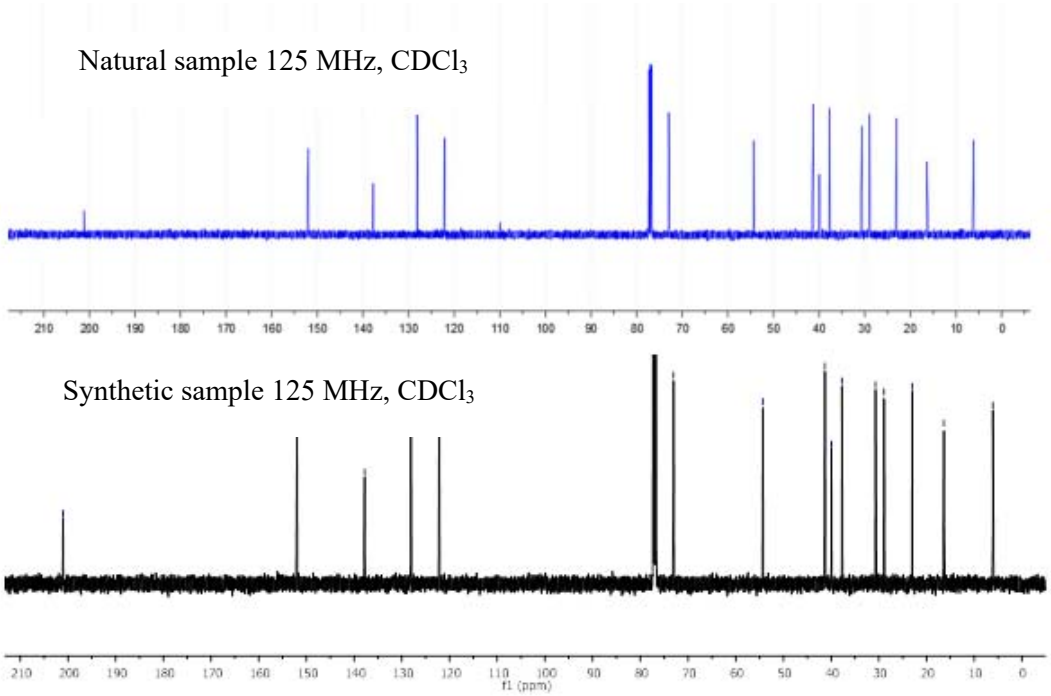
(-)-2,9-Humuladien-6-ol-8-one (3a)

Position	Reported ^{1}H δ (ppm); *J* (Hz)	Observed ^{1}H δ (ppm); *J* (Hz)	Δδ (ppm)	Reported ^{13}C δ (ppm)	Observed ^{13}C δ (ppm)	Δδ (ppm)
1a	1.86,dd(3.5,13.0)	1.86,dd(3.5,13.0)	0.00	41.3	41.3	0.0
1b	2.21,t(12.0)	2.21,t(12.0)	0.00			
2	5.08,d (3.5)	5.08,dd(3.5,11.0)	0.00	122.1	122.2	0.1
3				137.8	137.8	0.0
4a	1.95,brt(12.0)	1.95,t(12.0)	0.00	37.7	37.7	0.0
4b	2.07,dd(3.5,12.5)	2.07,dd(3.5,12.5)	0.00			
5a	1.11,m	1.11,m	0.00	30.6	30.7	0.1
5b	1.30,m	1.30,m	0.00			
6	4.22,m	4.22,m	0.00	73.0	73.0	0.0
7	2.91,m	2.90,m	0.01	54.3	54.3	0.0
8				201.5	201.0	0.5
9	6.10,d(16.0)	6.10,d(16.0)	0.00	128.1	128.1	0.0
10	6.15,d(16.0)	6.15,d(16.0)	0.00	152.0	152.0	0.0
11				40.0	40.0	0.0
12	1.37,s	1.37,s	0.00	16.4	16.4	0.0
13	1.03,s	1.03,d(6.5)	0.00	6.1	6.1	0.0
14	1.12,s	1.12,s	0.00	23.0	23.0	0.0
15	1.16,s	1.16,s	0.00	28.9	28.9	0.0

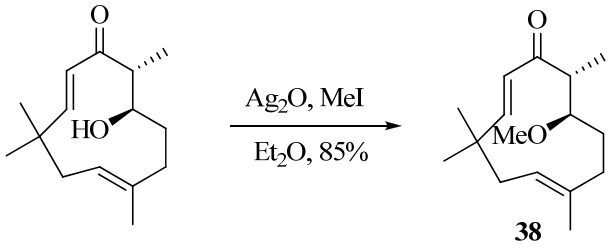
Comparison of ^{1}H NMR spectra of (-)-2,9-Humuladien-6-ol-8-one (3a)



Comparison of^{13}C NMR spectra of (-)-2,9-Humuladien-6-ol-8-one (3a):



7.6: Synthesis of compound 38:

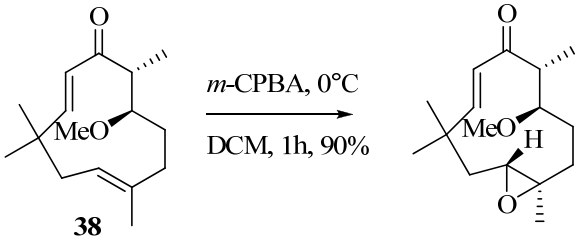


38

(-)-2,9-Humuladien-6-ol-8-one (3a)

To a solution of **3a** (47 mg, 0.2 mmol) in 2 mL of anhydrous diethyl ether were introduced molecular sieves 4 Å, Ag_2O (220 mg, 1 mmol) and MeI (0.16 mL, 2.6 mmol). The resulting reaction mixture was stirred for 24h at room temperature and filtered. The solvent was evaporated and the crude product was purified by column chromatography to afford **38** as a colorless liquid (0.17 mmol, 43mg, 85% yield). $[\alpha]_D^{25}$= -56.5 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.18 (d, *J* = 16.1 Hz, 1H), 6.06 (d, *J* = 16.1 Hz, 1H), 5.08 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.69 – 3.67 (m, 1H), 3.41 (s, 3H), 3.09 – 3.04 (m, 1H), 2.21 (t, *J* = 12.4 Hz, 1H), 2.10-2.06 (m, 1H), 1.90 – 1.84 (m, 2H), 1.41-1.37 (m, 1H), 1.36 (s, 3H), 1.17 (s, 3H), 1.14 (s, 3H), 1.06 – 1.00 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 3H).**^{13}CNMR {^{1}H}** (125 MHz, $CDCl_3$) δ 201.2, 151.6, 138.2, 128.0, 121.9, 82.3, 56.9, 49.3, 41.3, 40.0, 38.5, 28.9, 28.2, 22.9, 16.2, 6.12. **IR**: 2957, 2933, 2873, 1694, 1627, 1454, 1385, 1367, 1302, 1265, 1232, 1173, 1155, 1120, 1091,1057,1045,1000 cm^{-1}. **HRMS (ESI) m/z**: for $C_{16}H_{27}O_2[M + H]^+$, calculated: 251.2011; found: 251.2008.

7.7: Synthesis of (-)-alashanoid C (4b):

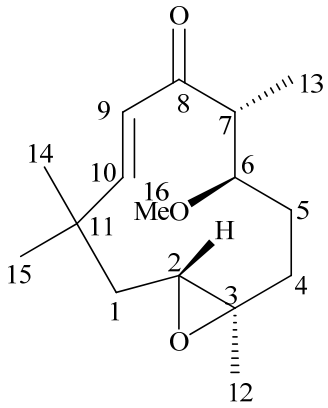


38

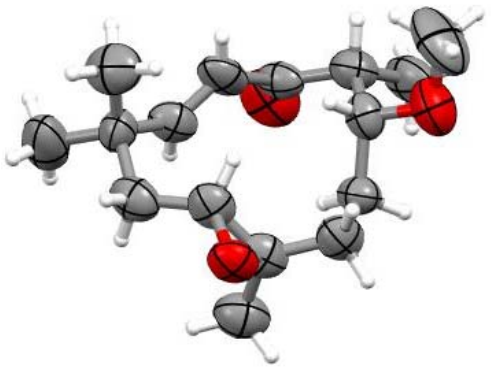
(-)Alashanoid C (4b)

To a cooled (0 °C) stirred solution of **38** (43 mg, 0.17 mmol) in CH_2Cl_2 (2 mL) was added *m*-CPBA (77%, 36 mg, 0.21mmol). After being stirred at 0 °C for 1h, the mixture was quenched with 10% aqueous $Na_2S_2O_3$ (3 mL) and extracted with CH_2Cl_2. The combined extracts were washed with saturated aqueous $NaHCO_3$ (5 mL), dried and concentrated under reduced pressure. The residue was purified by column chromatography to furnish the title compound (0.15 mmol, 40mg, 90% yield). $[\alpha]_D^{25}$= -140.2 (c = 0.1, MeOH).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.29 (s, 2H), 3.59 (dd, *J* = 8.5, 3.5 Hz, 1H), 3.38 (s, 3H), 3.10 (m, 1H), 2.71 (d, *J* = 11.0 Hz, 1H), 2.14 (dd, *J* = 14.0, 8.5 Hz, 1H), 1.92 (d, *J* = 14.0 Hz, 1H), 1.46 (m, 1H), 1.38 (dd, *J* = 14.0, 11.5 Hz, 1H), 1.28 (s, 3H), 1.16 (s, 3H), 1.10 (s, 3H), 1.06 (m, 1H), 0.97(d, *J*= 6.5Hz, 3H), 0.96 (overlap,1H). **^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 202.3,150.8,128.0, 83.6, 61.9, 60.8, 57.2, 48.2, 40.5, 37.4, 36.4, 29.7, 25.8, 23.5, 16.8, 6.0.**IR**: 2963, 2940, 2878, 1693, 1631, 1455, 1388, 1372, 1303, 1269, 1232, 1094, 1060, 1037, 1024, 1001, 983, 967, 913, 894, 677 cm^{-1}. **HRMS (ESI) m/z**: for $C_{16}H_{27}O_3[M + H]^+$, calculated: 267.1960; found: 267.1962.

NMR comparison data of natural and synthetic (-)-alashanoid C (4b):

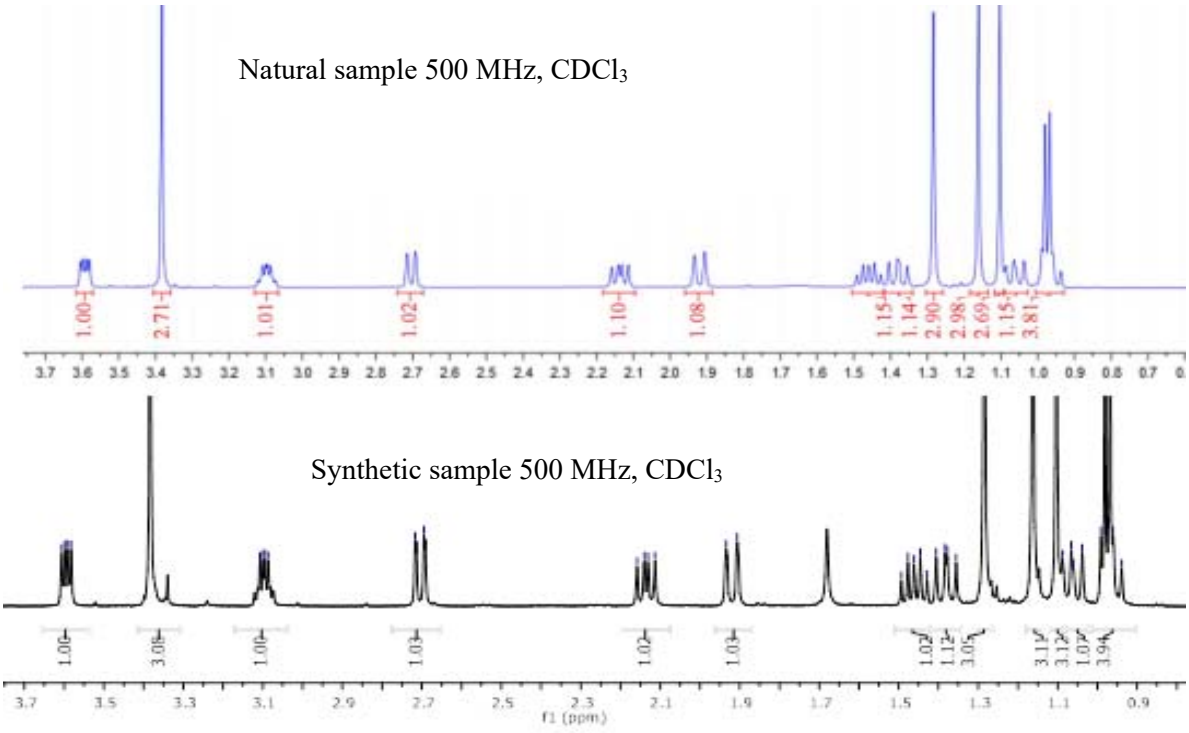


(-)Alashanoid C (4b)

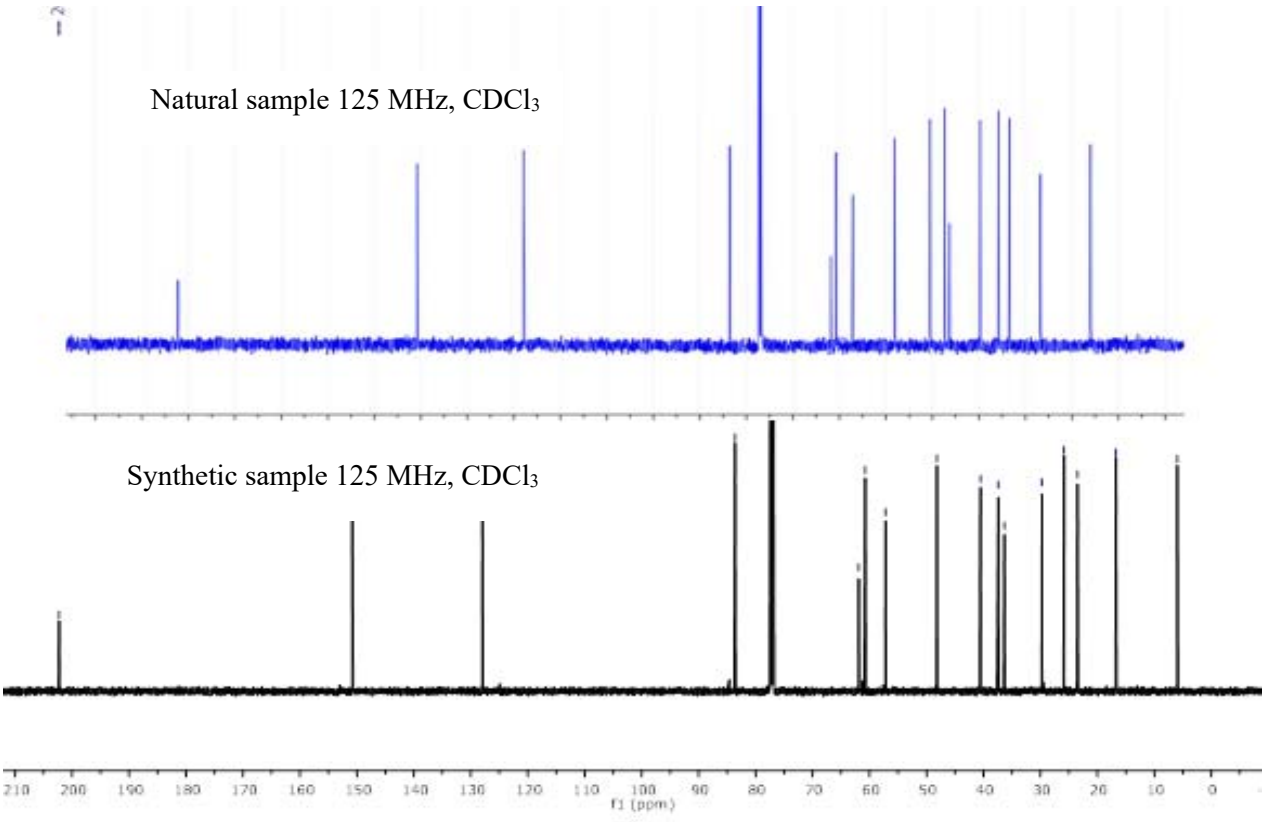


Position	Reported ^{1}H δ (ppm); *J* (Hz)	Observed ^{1}H δ (ppm); *J* (Hz)	Δδ (ppm)	Reported ^{13}C δ (ppm)	Observed ^{13}C δ (ppm)	Δδ (ppm)
1a	1.92,d(14.0)	1.92,d(14.0)	0.00	40.5	40.5	0.0
1b	1.38,dd(14.0,11.5)	1.38,dd(14.0,11.5)	0.00			
2	2.71,d(11.0)	2.71,d(11.0)	0.00	60.7	60.8	0.1
3				61.9	61.9	0.0
4a	1.06,m	1.06,m	0.00	37.4	37.4	0.0
4b	2.14,dd(14.0,8.5)	2.14,dd(14.0,8.5)	0.00			
5a	0.96,overlap	0.96,overlap	0.00	25.8	25.8	0.0
5b	1.46,m	1.46,m	0.00			
6	3.59,dd(8.5,3.5)	3.59,dd(8.5,3.5)	0.00	83.6	83.6	0.0
7	3.10,m	3.10,m	0.00	48.1	48.2	0.1
8				202.3	202.3	0.0
9	6.29,s	6.29,s	0.00	128.0	128.0	0.0
10	6.29,s	6.29,s	0.00	150.8	150.8	0.0
11				36.4	36.4	0.0
12	1.10,s	1.10,s	0.00	16.8	16.8	0.0
13	0.97,d(6.5)	0.97,d(6.5)	0.00	6.0	6.0	0.0
14	1.28,s	1.28,s	0.00	23.5	23.5	0.0
15	1.16,s	1.16,s	0.00	29.7	29.7	0.0
16	3.38,s	3.38,s	0.00	57.2	57.2	0.0

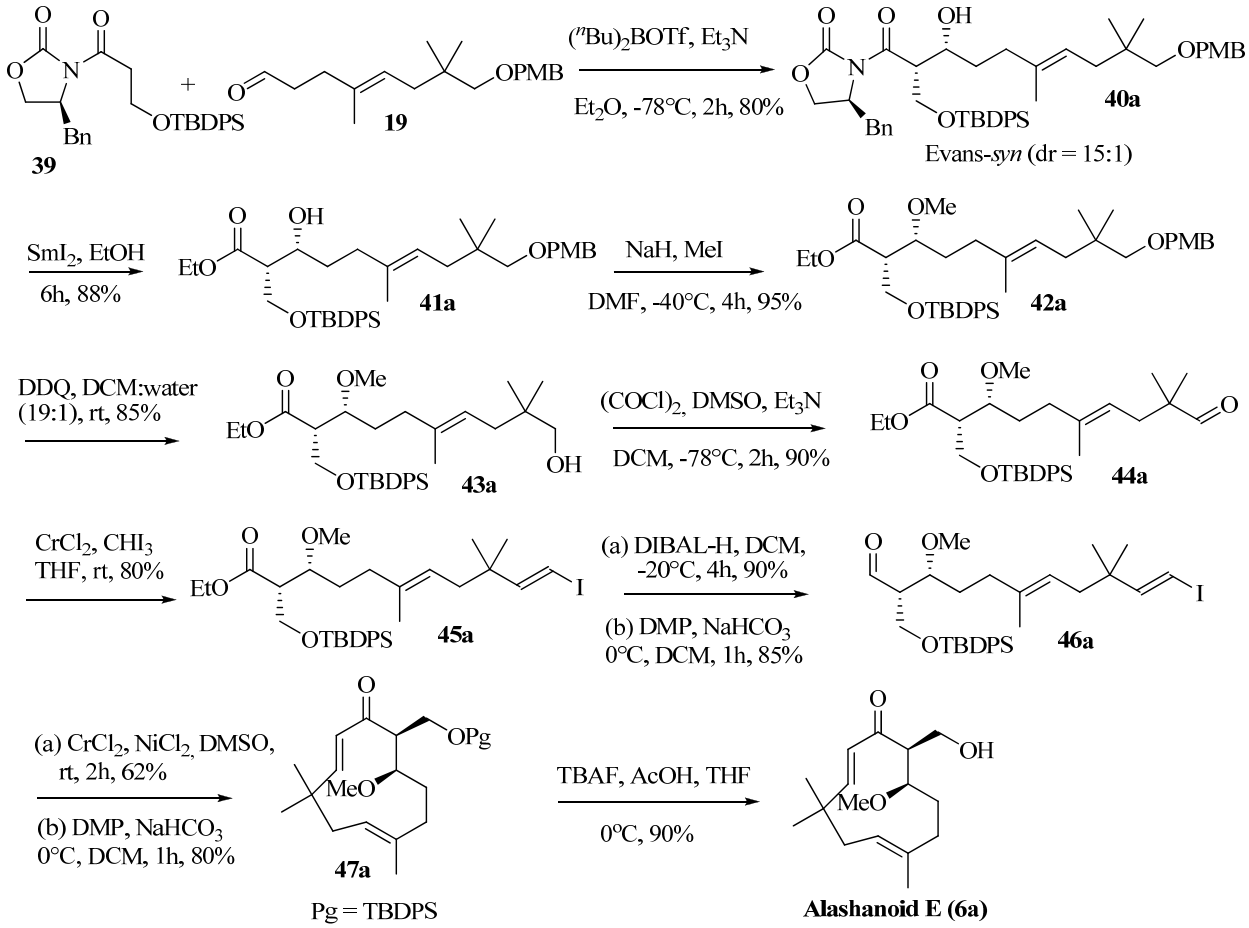
Comparison of ^{1}H NMR spectra of (-)-alashanoid C (4b)



Comparison of ^{13}C NMR spectra of (-)-alashanoid C (4b)

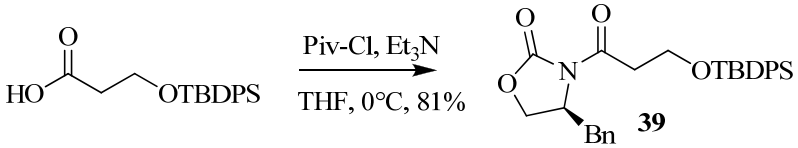


8: Synthesis of (+)-alashanoid E:



Scheme S6: Synthesis of **(+)-alashanoid E(6a).**

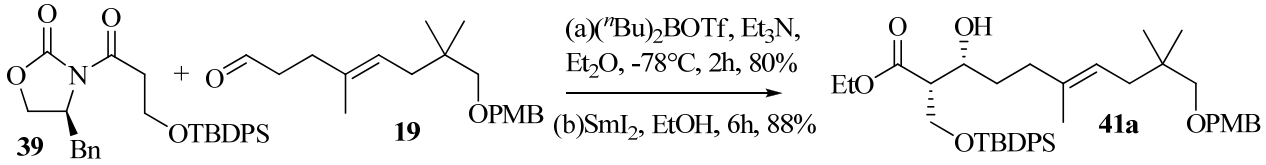
8.1. Synthesis of Auxiliary 39:



To a solution of 3-((tert-butyldiphenylsilyl)oxy)propanoic acid (2.5 g, 7.6 mmol) dissolved in anhydrous THF (45 mL) under N_2 atmosphere at 0 °C was added Et_3N (6.1 mL, 43.38 mmol). The reaction was cooled to 0 °C, and pivaloyl chloride (1.4 mL, 11.42 mmol) was added dropwise. The reaction was stirred at 0 °C for 2h. Then, LiCl (1.7g, 38.82 mmol) and (*R*)-4-benzyl-2-oxazolidinone (2.1 g, 11.46 mmol) were added, and the reaction was stirred at the same temperature for 4h. The reaction was then, quenched with saturated aqueous $NaHCO_3$, and further diluted with H_2O (60 mL). The reaction was then extracted with EtOAc (4 × 10 mL). The organic extracts were combined, dried over Na_2SO_4, and concentrated in vacuo. The crude compound was purified by column chromatography on silica gel to give compound **39** as 81% yield (3 g, 6.2 mmol).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74-7.71 (m, 3H), 7.47 – 7.40 (m, 5H), 7.36 – 7.22 (m, 7H), 4.72 – 4.68 (m, 1H), 4.22 – 4.16 (m, 2H), 4.09 (t, *J* = 6.2 Hz, 2H), 3.33 – 3.22 (m, 3H), 2.82-2.78 (m, 1H), 1.07 (s, 9H).**^{13}C NMR {^{1}H}** (125 MHz, $CDCl_3$) δ 171.2, 153.4, 135.6, 135.5, 135.3,

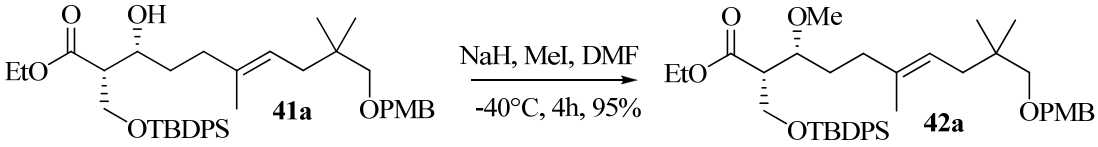
133.5, 129.6, 129.4, 128.9, 127.7, 127.3, 66.1, 59.5, 55.0, 38.5, 37.9, 26.8, 19.2. **IR**: 2956, 2919, 2851, 1457, 1247, 1018cm^{-1}. **HRMS (ESI) m/z**: for $C_{29}H_{34}NO_4Si$ $[M + H]^+$, calculated: 488.2257; found: 488.2253.

8.2. Synthesis of compound 41a:



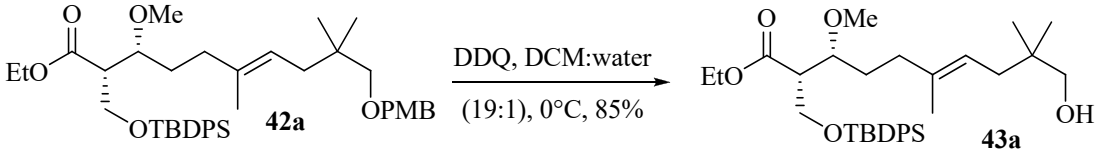
Compound **41a** (0.5 mmol, 332mg, 70% over 2 steps) was synthesized from **19** (0.82 mmol, 265mg) by employing Evans *syn* aldol protocol (**GPVB**) then followed by auxiliary removal according to **GPXIII** method. $[\alpha]_D^{25}$= +10.2(c = 0.1,MeOH).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57-7.53 (s, 4H), 7.34 – 7.27 (m, 6H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 5.08 (t, *J* = 7.6 Hz, 1H), 4.31 (s, 2H), 4.14 – 4.03 (m, 2H), 3.91-3.88 (m, 1H), 3.83 (dd, *J* = 10.1, 5.8 Hz, 1H), 3.78 (dd, *J* = 13.1, 4.8 Hz, 1H), 3.70 (s, 3H), 2.98 (s, 2H), 2.62 (dd, *J* = 11.9, 5.8 Hz, 1H), 2.09 – 2.03 (m, 1H), 1.98-1.92 (m, 1H), 1.86 (d, *J* = 7.7 Hz, 2H), 1.51 – 1.39 (m, 5H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.94 (s, 9H), 0.77 (s, 6H).**^{13}C NMR {^{1}H}** (125 MHz, $CDCl_3$) δ 173.6, 158.9, 136.1, 135.5, 135.5, 133.1, 133.1, 131.2, 129.7, 128.8, 127.7, 127.7, 121.4, 113.6, 78.8, 72.8, 69.7, 63.0, 60.6, 55.2, 53.2, 37.1, 36.1, 35.7, 33.7, 26.7, 24.5, 24.5, 19.2, 16.0, 14.2. **IR**: 3073, 2957, 2932, 2858, 1731, 1612, 1514, 1429, 1247, 1179, 1111, 1038, 823, 741, 704, 615, 504 cm^{-1}. **HRMS (ESI) m/z**: for $C_{40}H_{57}O_6Si$ $[M + H]^+$, calculated: 661.3924; found: 661.3919.

8.3. Synthesis of compound 42a:



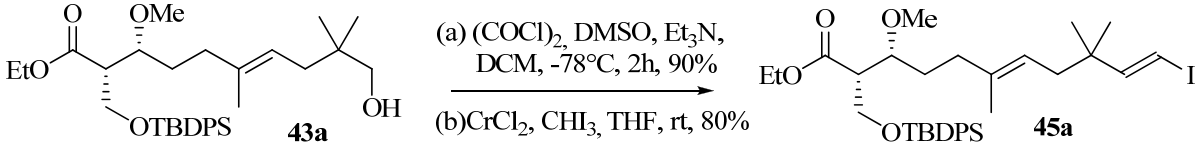
Compound **42a** (0.47 mmol, 330mg, 95% yield) was synthesized from **41a** (0.5 mmol, 332mg) by method as depicted above (**GPXIV**). $[\alpha]_D^{25}$= +4.0 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 – 7.55 (m, 4H), 7.32 – 7.25 (m, 6H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 5.01 (t, *J* = 7.4 Hz, 1H), 4.31 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.87 – 3.83 (m, 1H), 3.70 (s, 3H), 3.65 (dd, *J* = 10.0, 5.1 Hz, 1H), 3.37 – 3.33 (m, 1H), 3.18 (s, 3H), 2.97 (s, 2H), 2.77 – 2.73 (m, 1H), 1.89 – 1.83 (m, 4H), 1.54 – 1.47 (m, 1H), 1.41 (s, 3H), 1.34-1.26 (m, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.93 (s, 9H), 0.75 (s, 6H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 172.8, 158.9, 136.1, 136.0, 135.5, 133.4, 133.3, 131.2, 129.7, 129.6, 128.8, 127.6, 121.2, 113.6, 79.1, 78.8, 72.8, 61.9, 60.3, 57.8, 55.2, 52.3, 37.1, 35.7, 35.1, 29.9, 26.9, 26.7, 24.5, 24.4, 19.1, 16.0, 14.3. **IR**: 3071, 2955, 2928, 2856, 1732, 1612, 1513, 1464, 1428, 1247, 1178, 1091, 1037, 822, 740, 702, 615, 504 cm^{-1}. **HRMS (ESI) m/z**: for $C_{41}H_{62}NO_6Si$ $[M + NH_4]^+$, calculated: 692.4346; found: 692.4343.

8.4. Synthesis of compound 43a:



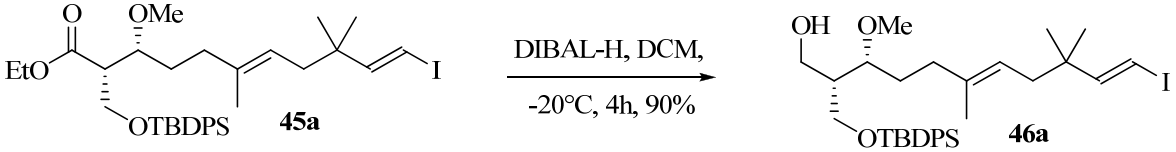
Compound **43a** (0.4 mmol, 226mg, 85% yield) was synthesized from **42a** (0.47 mmol, 330mg) by general method as described earlier (**GPVIII**). $[\alpha]_D^{25}$= +9.5 (c = 0.1, MeOH).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.0 Hz, 4H), 7.32 – 7.26 (m, 6H), 5.06 (t, *J* = 7.5 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.86 (t, *J* = 9.2 Hz, 1H), 3.66 (dd, *J* = 10.0, 4.9 Hz, 1H), 3.36 (dd, *J* = 10.8, 6.9 Hz, 1H), 3.19 (s, 5H), 2.76 (dd, *J* = 12.8, 7.5 Hz, 1H), 1.94 – 1.86 (m, 2H), 1.82 (d, *J* = 7.6 Hz, 2H), 1.44 (s, 3H), 1.36 – 1.28 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.93 (s, 9H), 0.75 (s, 6H).**^{13}C NMR {^{1}H}** (125 MHz, $CDCl_3$) δ 172.8, 136.5, 135.5, 133.4, 133.3, 129.7, 129.6, 127.6, 120.9, 79.1, 71.8, 61.8, 60.4, 57.8, 52.2, 36.8, 36.2, 35.1, 29.8, 26.7, 23.8, 19.1, 16.0, 14.2. **IR**:3750,2916,2851,1456cm^{-1}. **HRMS (ESI) m/z:** for $C_{33}H_{51}O_5Si[M + H]^+$, calculated: 555.3506; found: 555.3501.

8.5. Synthesis of compound 45a:



Compound **(*E*)-45a** (0.3 mmol, 200mg, 72% yield over 2 steps) was synthesized from **43a** (0.4 mmol, 226mg) by general method as described earlier (**GPI and GPXI**). $[\alpha]_D^{25}$= +11.0 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62-7.58 (m, 4H), 7.37 – 7.29 (m, 6H), 6.41 (d, *J* = 14.6 Hz, 1H), 5.81 (d, *J* = 14.6 Hz, 1H), 4.98 (t, *J* = 7.2 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.88 (t, *J* = 9.3 Hz, 1H), 3.68 (dd, *J* = 9.9, 5.1 Hz, 1H), 3.37 (dd, *J* = 8.9, 5.0 Hz, 1H), 3.22 (s, 3H), 2.80 – 2.76 (m, 1H), 1.92 – 1.73 (m, 4H), 1.57 – 1.48 (m, 1H), 1.42 (s, 3H), 1.38-1.29 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.95 (s, 9H), 0.88 (s, 6H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 172.7, 155.6, 137.0, 136.0, 135.5, 133.4, 133.4, 129.7, 129.6, 127.6, 127.5, 127.4, 120.4, 79.1, 72.3, 61.8, 60.3, 57.8, 52.2, 41.6, 40.2, 35.0, 30.0, 26.9, 26.7, 26.1, 26.0, 19.1, 16.0, 14.3. **IR**: 3071, 2958, 2932, 2859, 1732, 1428, 1181, 1106, 953, 822, 740, 702, 614, 504 cm^{-1}. **HRMS(ESI)m/z**: for $C_{34}H_{50}IO_4Si[M + H]^+$, calculated: 677.2523; found: 677.2520.

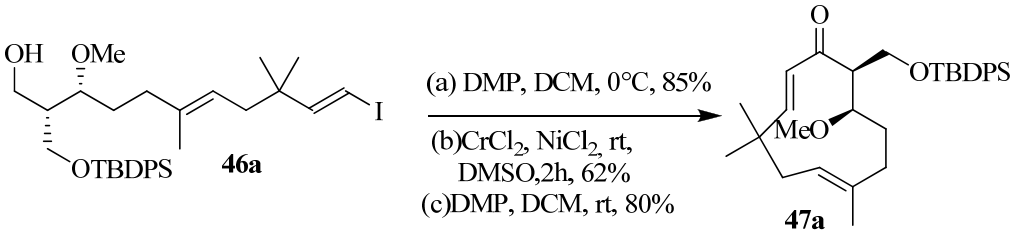
8.6. Synthesis of compound 46a:



Compound **46a** (0.26 mmol, 160mg, 90% yield) was synthesized from **45a** (0.3 mmol, 200mg) by general method as described earlier (**GPXIV**). $[\alpha]_D^{25}$= +15.3 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (t, *J* = 56.5 Hz, 4H), 7.37-7.30 (m, 6H), 6.42 (d, *J* = 14.6 Hz, 1H), 5.82 (d, *J* = 14.6 Hz, 1H), 5.02 (t, *J* = 7.1 Hz, 1H), 3.84 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.78 – 3.69 (m, 3H), 3.33 (dd, *J* = 11.1, 5.6 Hz, 1H), 3.24 (s, 3H), 1.90 (dd, *J* = 15.5, 7.6 Hz, 3H), 1.83-1.78 (m, 1H), 1.60 – 1.49 (m, 2H), 1.47(s, 3H), 0.99 (s, 9H), 0.89 (s, 6H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 155.6, 137.1, 135.6, 133.3, 129.7, 129.7, 127.7, 120.4, 81.2, 72.3, 63.8, 62.8, 57.9, 45.5, 41.6, 40.2, 35.4, 29.8, 26.9, 26.1, 26.0, 19.2, 16.1. **IR**:3073, 2958, 2926,

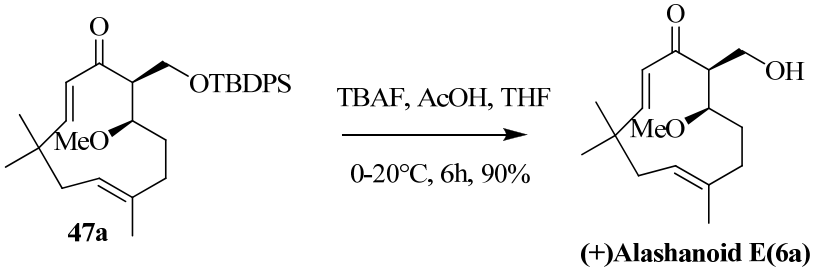
2855, 1733, 1464, 1428, 1113, 1084, 953, 825, 740, 702, 613, 505cm^{-1}. **HRMS (ESI) m/z**: for $C_{32}H_{48}IO_3Si[M + H]^+$, calculated: 635.2417; found: 677.2402.

8.7. Synthesis of compound 47a:



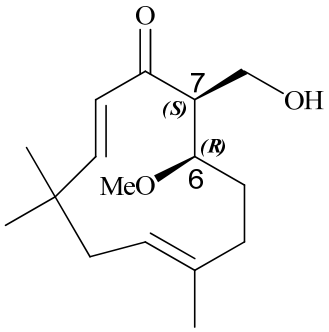
Compound **47a** (0.033 mmol, 17mg, 50% yield over 3 steps) was synthesized from **46a** (0.26 mmol, 160mg) general method as described earlier (**GPX** and **GPXII**). $[\alpha]_D^{25}$= +27.0 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 4H), 7.44 – 7.38 (m, 6H), 6.27 (d, *J* = 16.1 Hz, 1H), 6.09 (d, *J* = 16.1 Hz, 1H), 5.08 (dd, *J* = 11.3, 4.6 Hz, 1H), 4.24 – 4.20 (m, 1H), 3.77 (dd, *J* = 10.1, 3.0 Hz, 1H), 3.63 – 3.61 (m, 1H), 3.36 (s, 3H), 3.33-3.30 (m, 1H), 2.27 (t, *J* = 12.3 Hz, 1H), 2.04 (dd, *J* = 12.7, 6.7 Hz, 1H), 1.91 (dd, *J* = 13.2, 4.8 Hz, 1H), 1.80 (t, *J* = 12.2 Hz, 1H), 1.63 (s, 1H), 1.40 (s, 3H), 1.33 – 1.27 (m, 1H), 1.21 (s, 3H), 1.19 (s, 3H), 1.06 (s, 9H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 198.8, 152.6, 138.0, 135.7, 135.6, 134.1, 133.8, 129.4, 128.0, 127.5, 127.5, 122.0, 81.2, 57.6, 57.3, 57.1, 41.3, 40.0, 38.5, 28.7, 28.6, 26.8, 23.1, 19.2, 16.3. **IR**: 2959, 2918, 2850, 2020, 1733, 1464, 506cm^{-1}. **HRMS (ESI) m/z**: for $C_{32}H_{45}O_3Si[M + H]^+$, calculated: 505.3138; found: 505.3138.

8.8. Synthesis of (+) alashanoid E (6a):



Alashanoid E (0.03 mmol, 8mg, 90% yield) was synthesized from compound **47a** (0.033 mmol, 17mg) through a general method as described earlier (**GPXVI**). $[\alpha]_D^{25}$= +19.0 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.23 (d, *J* = 16.0 Hz, 1H), 6.05 (d, *J* = 16.0 Hz, 1H), 5.08 (dd, *J* = 11.5, 4.0 Hz, 1H), 3.98 (dd, *J* = 12.0, 8.0 Hz, 1H), 3.77 (dd, *J* = 13.5, 4.5 Hz, 1H), 3.72 (dd, *J* = 5.5, 4.0 Hz, 1H), 3.45 (s, 3H), 3.26 (m, 1H), 2.22 (t, *J* = 14.0 Hz, 1H), 2.12 (dd, *J* = 14.0, 7.0 Hz, 1H), 1.86 (overlap, 2H), 1.48 (m, 1H), 1.37 (s, 3H), 1.21 (overlap, 1H), 1.18(s,3H),1.14 (s, 3H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 201.0, 152.9, 138.1, 127.8, 122.2, 82.3, 58.1, 57.6, 56.6, 41.3, 40.3, 39.0, 29.0, 23.1, 16.4. **IR**: 3464, 2955, 2929, 2855, 1690, 1658, 1625, 1456, 1386, 1367, 1303, 1215, 1105, 1081, 1033, 1000cm^{-1}. **HRMS (ESI) m/z**: for $C_{16}H_{27}O_3[M + H]^+$, calculated: 267.1960; found: 267.1961.

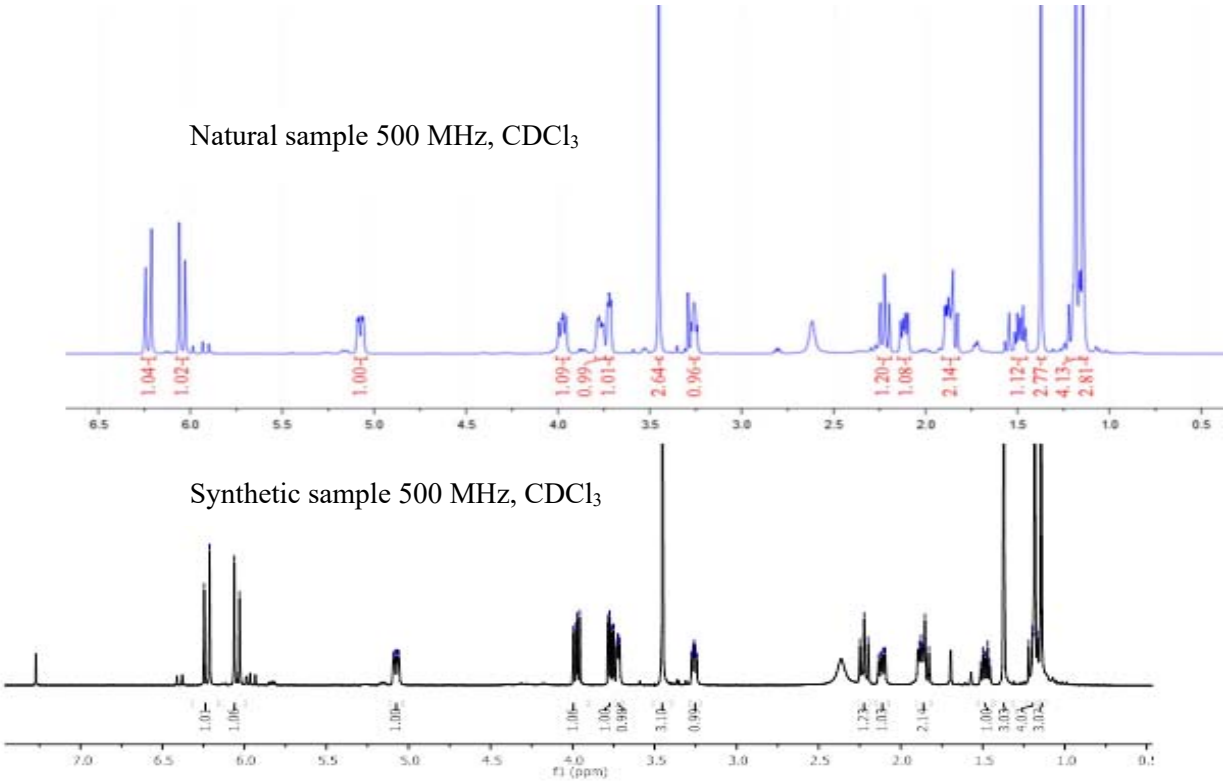
NMR comparison data of natural and synthetic (+)-alashanoid E (6a):



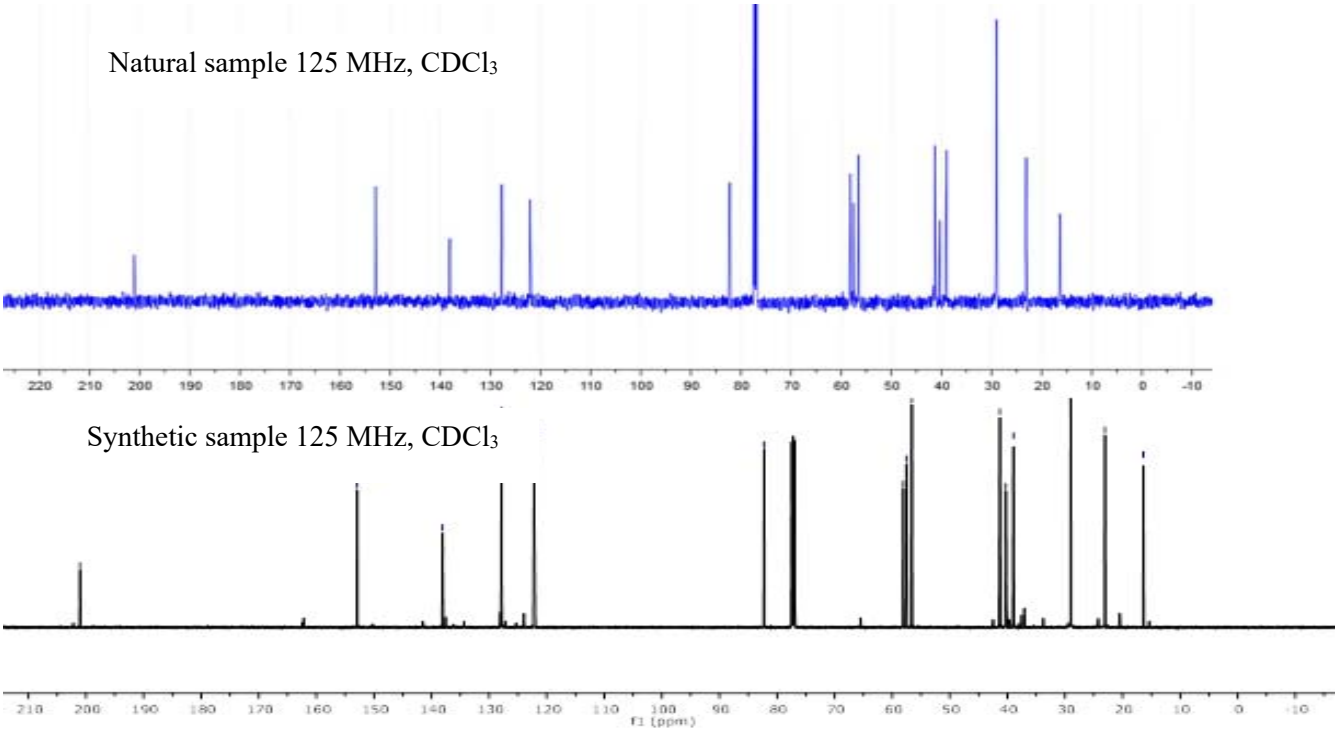
(+)Alashanoid E(6a)

Position	Reported ^{1}H δ (ppm); *J* (Hz)	Observed ^{1}H δ (ppm); *J* (Hz)	Δδ (ppm)	Reported ^{13}C δ (ppm)	Observed ^{13}C δ (ppm)	Δδ (ppm)
1a	2.22,t(14.0)	2.22,t(14.0)	0.00	41.3	41.3	0.0
1b	1.86(overlap)	1.86(overlap)	0.00			
2	5.07,dd(4.0,11.5)	5.08,dd(4.0,11.5)	0.01	122.1	122.2	0.1
3				138.1	138.1	0.0
4a	2.12,dd(7.0,14.0)	2.12,dd(7.0,14.0)	0.00	39.0	39.0	0.0
4b	1.86(overlap)	1.86(overlap)	0.00			
5a	1.48,m	1.48,m	0.00	29.0	29.0	0.0
5b	1.21(overlap)	1.21(overlap)	0.00			
6	3.72,dd(4.0,5.5)	3.72,dd(4.0,5.5)	0.00	82.3	82.3	0.0
7	3.26,m	3.26,m	0.00	57.6	57.6	0.0
8				201.1	201.0	0.1
9	6.04,d(16.0)	6.05,d(16.0)	0.01	127.8	127.8	0.0
10	6.23,d(16.0)	6.23,d(16.0)	0.00	152.9	152.9	0.0
11				40.3	40.3	0.0
12	1.37,s	1.37,s	0.00	16.4	16.4	0.0
13a	3.77,dd(4.5,13.5)	3.77,dd(4.5,13.5)	0.00	58.2	58.1	0.1
13b	3.98,dd(8.0,12.0)	3.98,dd(8.0,12.0)	0.00			
14	1.14,s	1.14,s	0.00	23.1	23.1	0.0
15	1.18,s	1.18,s	0.00	29.0	29.0	0.0
16	3.45,s	3.45,s	0.00	56.5	56.6	0.1

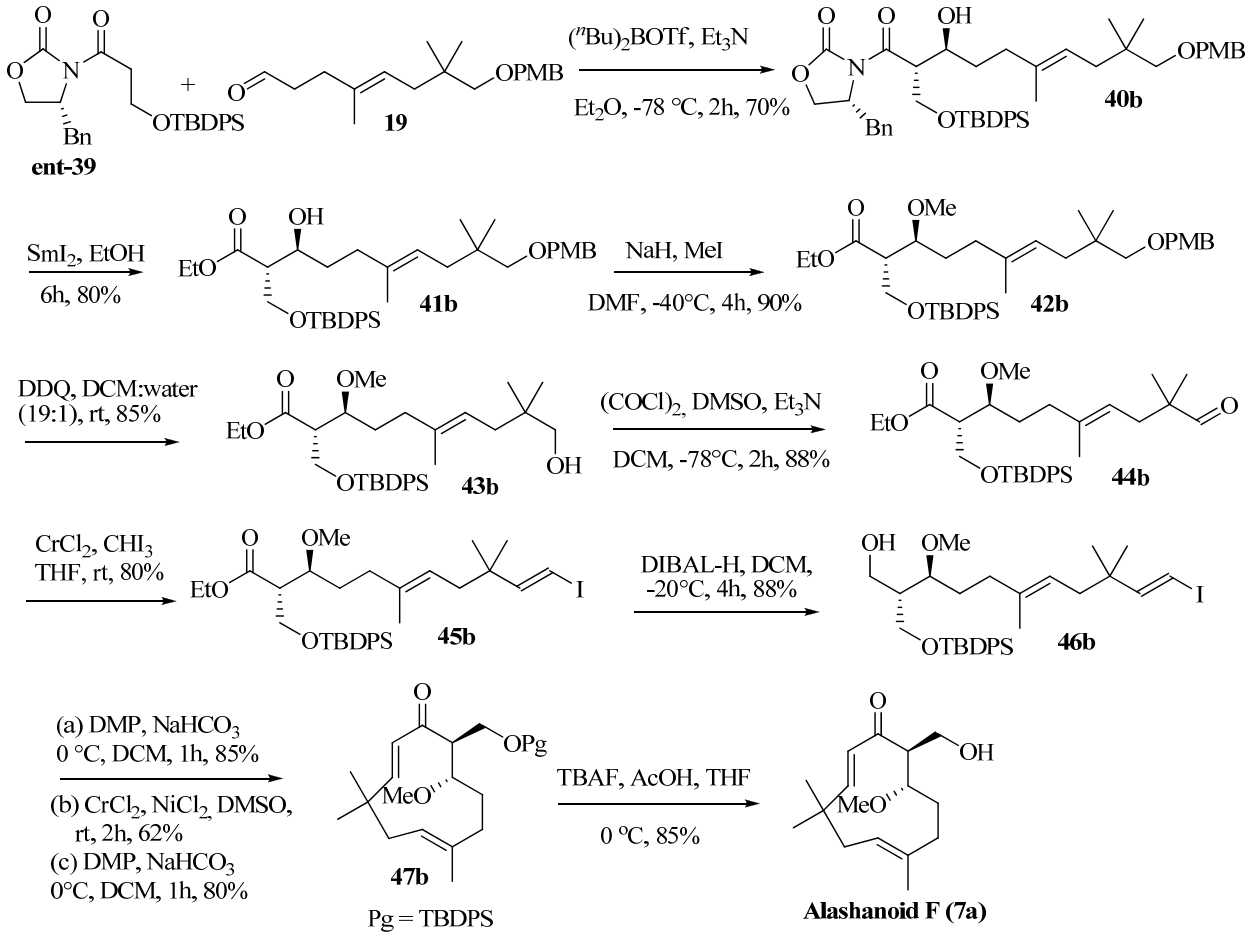
Comparison of ^{1}H NMR spectra of (+)-alashanoid E (6a):



Comparison of ^{13}C NMR spectra of (+)-alashanoid E (6a):

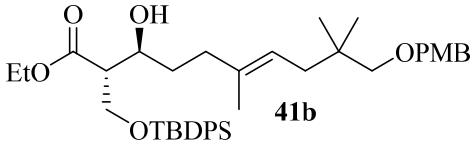


9: Synthesis of (+) alashanoid F (7a):



Scheme S7: Synthesis of **(+) alashanoid F(7a).**

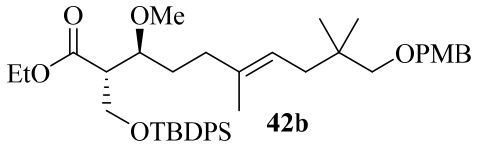
9.1. Synthesis of compound 41b:



Compound **41b** (1.66 mmol, 1.1g, 56% yield over 2 steps) was synthesized from **ent-39** (2.02 mmol, 985mg) and aldehyde **19** (2.63mmol, 800mg) by non-Evans *anti*-aldol protocol as described earlier (**GPVA**) and then the auxiliary was removed by the method described in **GPXIII**. $[\alpha]_D^{25}$= +4.9 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66-7.63 (m, 4H), 7.42 – 7.35 (m, 6H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.16 (t, *J* = 7.7 Hz, 1H), 4.39 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.04-3.97 (m, 2H), 3.95-3.91 (m, 1H), 3.77 (s, 3H), 3.06 (s, 2H), 2.69 (q, *J* = 6.2 Hz, 1H), 2.18 – 2.12 (m, 1H), 2.04 – 1.98 (m, 1H), 1.94 (d, *J* = 7.7 Hz, 2H), 1.54 – 1.50 (m, 5H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.02 (s, 9H), 0.84 (s, 6H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 173.1, 158.9, 136.1, 135.6, 135.5, 133.0, 133.0, 131.2, 129.8, 128.8, 127.7, 127.7, 121.5, 113.6, 78.8, 72.8, 70.8, 62.6, 60.6, 55.2, 53.2, 37.1, 36.1, 35.7, 33.3, 26.7, 24.5, 24.5, 19.1, 16.0, 14.2. **IR**: 3043, 2977, 2912, 2828, 1761, 1642, 1524, 1469, 1207, 1129, 1134,

1012, 803, 764, 710, 623, 514 cm^{-1}. **HRMS (ESI) m/z**: for $C_{40}H_{57}O_6Si$ $[M + H]^+$, calculated: 661.3924; found: 661.3927.

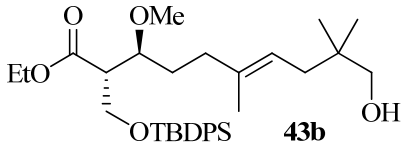
9.2. Synthesis of compound 42b:



42b

Compound **42b** (0.15 mmol, 100mg, 90% yield) was synthesized from **41b** (0.166 mmol, 110mg) by employing the general method as described earlier (**GPXIV**). $[\alpha]_D^{25}$= +2.0 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 4H), 7.46 – 7.39 (m, 6H), 7.27 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 5.20 (t, *J* = 7.7 Hz, 1H), 4.45 (s, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.09 – 4.05 (m, 1H), 3.92 (dd, *J* = 9.9, 4.9 Hz, 1H), 3.83 (s, 3H), 3.49 (dd, *J* = 7.4, 3.6 Hz, 1H), 3.27 (s, 3H), 3.11 (s, 2H), 2.94-2.90 (m, 1H), 2.16 – 2.11 (m, 1H), 2.05 – 1.98 (m, 3H), 1.62 – 1.59 (m, 5H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.06 (s, 9H), 0.90 (s, 6H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 172.7, 158.9, 136.2, 135.6, 135.5, 133.5, 133.5, 131.2, 129.6, 129.6, 128.8, 127.6, 127.6, 121.2, 113.6, 78.8, 78.8, 72.8, 62.6, 60.3, 57.3, 55.2, 52.4, 37.1, 35.7, 35.2, 30.5, 26.7, 24.5, 24.5, 19.2, 16.0, 14.2. **IR**: 3051, 2946, 2913, 2834, 1745, 1632, 1554, 1443, 1404, 1224, 1139, 1071, 1024, 812, 720, 702, 645, 510 cm^{-1}. **HRMS (ESI) m/z**: for $C_{41}H_{62}NO_6Si$ $[M + NH_4]^+$, calculated: 692.4346; found: 692.4341.

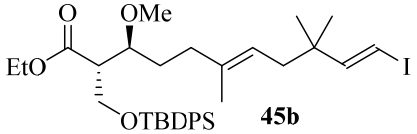
9.3. Synthesis of compound 43b:



43b

Compound **43b** (0.127 mmol, 70.6mg, 85% yield) was synthesized from **42b** (0.15 mmol, 100mg) by employing the general method as described earlier (**GPVIII**). $[\alpha]_D^{25}$= +6.4 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69– 7.67 (m, 4H), 7.46 – 7.38 (m, 6H), 5.23 (t, *J* = 7.7 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.08 – 4.04 (m, 1H), 3.91 (dd, *J* = 9.8, 4.9 Hz, 1H), 3.51-3.47 (m, 1H), 3.33 (s, 2H), 3.27 (s, 3H), 2.93-2.88 (m, 1H), 2.17 – 2.13 (m, 1H), 2.06 – 1.99 (m, 1H), 1.97 (d, *J* = 7.7 Hz, 2H), 1.65-1.56 (d, *J* = 25.1 Hz, 5H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.05 (s, 9H), 0.89 (s, 6H).**^{13}C NMR {^{1}H}** (125 MHz, $CDCl_3$) δ 172.7, 166.4, 141.1, 136.6, 136.5, 135.5, 135.5, 133.5, 133.5, 129.6, 129.6, 127.6, 124.4, 121.0, 120.9, 78.7, 71.8, 62.5, 60.4, 57.3, 52.4, 36.8, 36.2, 35.2, 34.5, 30.4, 26.7, 23.8, 19.2, 16.0, 14.2. **IR**:3710,2986,2851,2810,1495,1416cm^{-1}. **HRMS (ESI) m/z:** for $C_{33}H_{51}O_5Si[M + H]^+$, calculated: 555.3506; found: 555.3503.

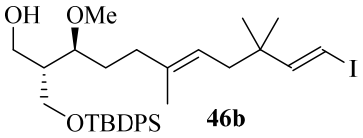
9.4. Synthesis of compound 45b:



45b

Compound (*E*)-**45b** (0.089 mmol, 60.5mg, 70% yield over 2 steps) was synthesized from **43b** (0.127 mmol, 70.6mg) by employing the general method as described earlier (**GPXI**). $[\alpha]_D^{25}$= +8.2 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59-7.57 (m, 4H), 7.36-7.29 (m, 6H), 6.42 (d, *J* = 14.6 Hz, 2H), 5.82 (d, *J* = 14.6 Hz, 2H), 5.03 (t, *J* = 7.2 Hz, 2H), 4.10 (q, *J* = 7.1 Hz,, 2H), 3.99 – 3.95 (m, 1H), 3.81 (dd, *J* = 9.8, 4.9 Hz, 1H), 3.37 (dd, *J* = 7.4, 3.5 Hz, 1H), 3.18 (s, 3H), 2.84-2.79 (m, 1H), 2.07 – 2.01 (m, 1H), 1.95 – 1.88 (m, 3H), 1.55 – 1.47 (m, 5H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.96 (s, 9H), 0.90 (s, 6H).**^{13}C NMR {^{1}H}** (125 MHz, $CDCl_3$) δ 172.7, 155.7, 137.1, 135.6, 135.5, 133.5, 133.5, 129.6, 129.6, 127.6, 120.4, 78.7, 72.3, 62.6, 60.4, 57.3, 52.4, 41.6, 40.2, 35.1, 30.4, 26.7, 26.1, 19.2, 16.1, 14.3. **IR**: 3042, 2908, 2902, 2819, 1752, 1458, 1111, 1100, 993, 828, 743, 710, 614, 502 cm^{-1}. **HRMS(ESI)m/z**: for $C_{34}H_{50}IO_4Si[M + H]^+$, calculated: 677.2523; found: 677.2525.

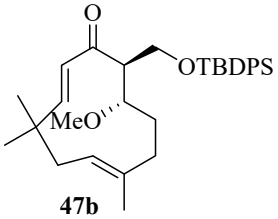
9.5. Synthesis of compound 46b:



46b

Compound **46b** (0.078 mmol, 50mg, 88% yield) was synthesized from **45b** (0.089 mmol, 60.5mg) by employing the general method as described earlier (**GPXV**). $[\alpha]_D^{25}$= +13.1(c = 0.1,MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 4H), 7.38 – 7.32 (m, 6H), 6.42 (d, *J* = 14.6 Hz, 1H), 5.82 (d, *J* = 14.6 Hz, 1H), 5.02 (t, *J* = 7.5 Hz, 1H), 3.79-3.65 (m, 4H),3.30- 3.25 (m, 1H), 3.23 (s, 3H), 2.05 – 1.96 (m, 2H), 1.93-1.88 (m, 3H), 1.53 – 1.40 (m, 4H), 0.99 (s, 9H), 0.90 (s, 6H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 155.6, 137.1, 135.6, 135.5, 133.2, 133.1, 129.8, 129.8, 127.7, 127.7, 120.4, 80.6, 72.3, 63.4, 63.4, 57.5, 44.5, 41.6, 40.2, 35.7, 28.8, 26.8, 26.1, 19.1, 16.1. **IR**:3045, 2978, 2906, 2865, 1710, 1442, 1408, 1153, 1014, 945, 835, 720, 702, 619, 507cm^{-1}. **HRMS (ESI) m/z**: for $C_{32}H_{48}IO_3Si[M + H]^+$, calculated: 635.2417; found: 677.2405.

9.6. Synthesis of compound 47b:



47b

Compound **47b** (0.033 mmol, 16 mg, 42% yield over 3 steps) was synthesized from **46b** (0.078 mmol, 50mg) by employing the general method as described earlier (**GPX and GPXII**). $[\alpha]_D^{25}$= +25.9 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 4H), 7.33 – 7.25 (m, 6H), 6.15 (d, *J* = 16.3 Hz, 1H), 6.05 (d, *J* = 16.3 Hz, 1H), 5.03 (dd, *J* = 11.5, 4.2 Hz, 1H), 4.04 – 4.00 (m, 1H), 3.87 – 3.84 (m, 1H), 3.36 (dd, *J* = 7.7, 3.7 Hz, 1H), 3.13 (s, 3H), 2.67-2.63 (m, 1H), 2.12 (dd, *J* = 20.6, 8.4 Hz, 2H), 1.89 (t, *J* = 11.4 Hz, 1H), 1.80 – 1.77 (m, 1H), 1.57 – 1.42 (m, 2H), 1.36 (s, 3H), 1.10 (s, 3H), 1.03 (s, 3H), 0.93 (s, 9H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 202.1, 153.4, 137.4, 135.7, 135.6, 133.4, 133.4, 129.6, 129.6, 127.6, 127.6, 127.0, 122.8, 80.1, 61.6, 61.5, 56.9, 41.1, 39.6, 31.7, 29.1, 26.8, 23.5, 19.2, 16.1. **IR**: 2979, 2928, 2832, 2065, 1717, 1434, 508cm^{-1}. **HRMS (ESI) m/z**: for $C_{32}H_{45}O_3Si[M + H]^+$, calculated: 505.3138; found: 505.3139.

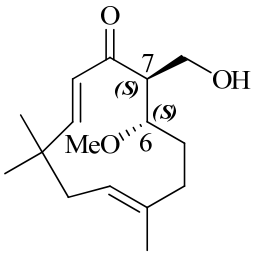
9.7. Synthesis of (+)-alashanoid F (7a):

Alashanoid F (0.0175 mmol, 5mg, 85% yield) was synthesized from compound **47b** (0.0225 mmol, 12.5mg) by employing the general method as described earlier (**GPXVI**). $[\alpha]_D^{25}$= +18.4 (c = 0.1, MeOH).

^{1}H NMR

(500 MHz, $CDCl_3$) δ 6.25 (d, *J* = 16.5 Hz, 1H), 5.92 (d, *J* = 16.5 Hz, 1H), 5.17 (dd, *J* = 11.5, 4.5 Hz, 1H), 4.02 (dd, *J* = 11.5, 7.0 Hz, 1H), 3.88 (dd, *J* = 12.0, 5.5 Hz, 1H), 3.54 (m, 1H), 3.30 (s, 3H), 2.82 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.33 – 2.21 (overlap, 2H), 2.00 (m, 1H), 1.92 (dd, *J* = 13.5, 4.5 Hz, 1H), 1.75 – 1.72 (m, 2H), 1.56 (s, 3H), 1.17 (s, 3H), 1.16 (s,3H). **^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 203.2, 155.5, 137.0, 126.3, 123.7, 82.4, 60.8, 60.4, 57.5, 41.6, 39.8, 39.2, 32.5, 28.9,23.8, 16.5. **IR**: 3437, 2957, 2932, 2872, 2855, 1686, 1621, 1461, 1386,1366,1216, 1175, 1105, 1083, 1059, 1001, 754cm^{-1}. **HRMS (ESI) m/z**: for $C_{16}H_{27}O_3[M + H]^+$, calculated: 267.1960; found: 267.1964.

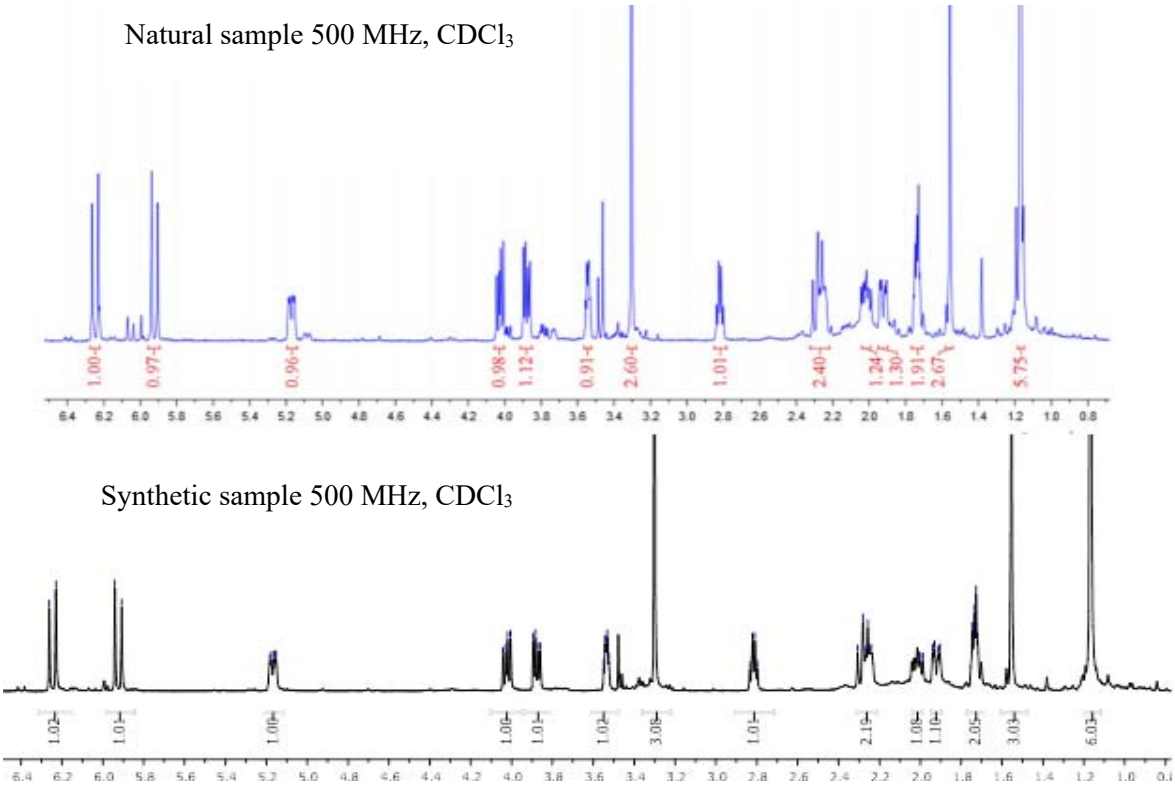
NMR comparison data of natural and synthetic (+)-alashanoid F (7a):



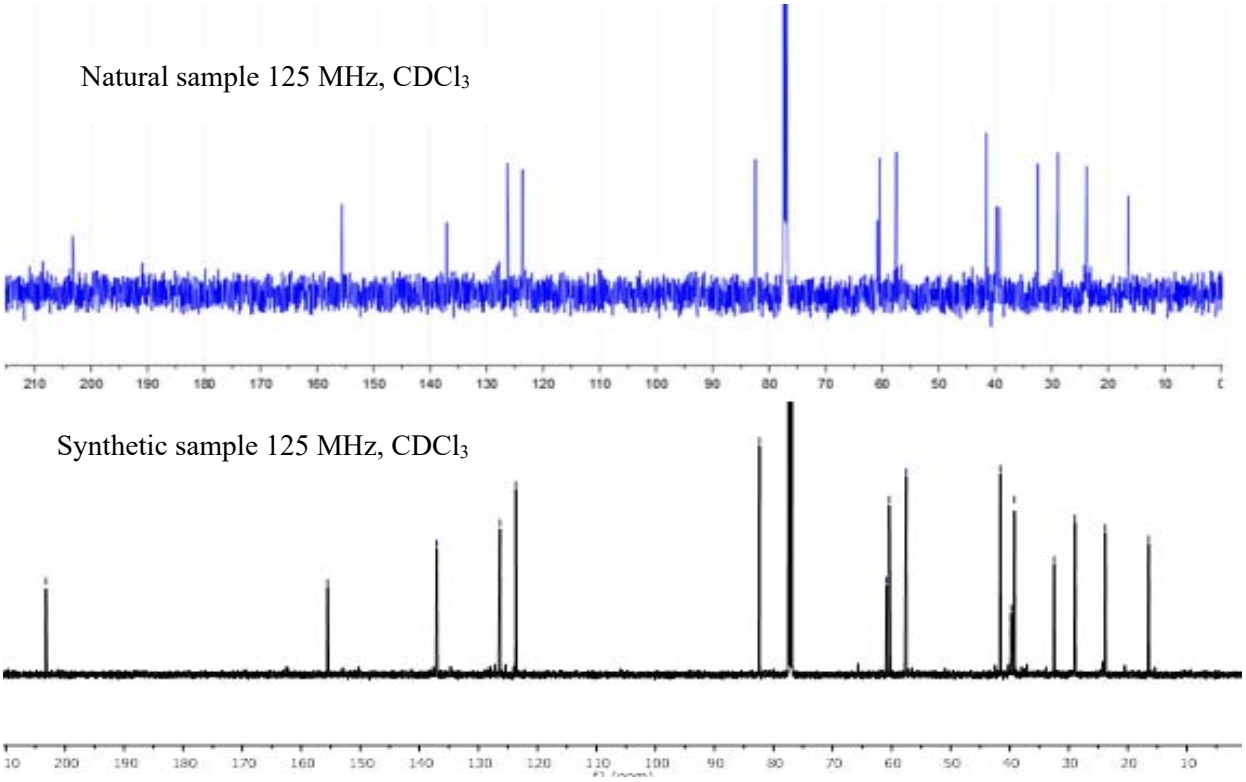
(+)Alashanoid F(7a)

Position	Reported ^{1}H δ (ppm); *J* (Hz)	Observed ^{1}H δ (ppm); *J* (Hz)	Δδ (ppm)	Reported ^{13}C δ (ppm)	Observed ^{13}C δ (ppm)	Δδ (ppm)
1a	2.33(overlap)	2.33,overlap	0.00	41.6	41.6	0.0
1b	1.92,dd(4.5,13.5)	1.92,dd(4.5,13.5)	0.00			
2	5.17,dd(4.5,11.5)	5.17,dd(4.5,11.5)	0.00	123.6	123.7	0.1
3				137.0	137.0	0.0
4a	2.23(overlap)	2.23,overlap	0.00	39.8	39.8	0.0
4b	2.00,m	2.00,m	0.00			
5	1.72-1.75,m	1.72-1.75,m	0.00	32.5	32.5	0.0
6	3.54,m	3.54,m	0.00	82.4	82.4	0.0
7	2.82,q(6.0)	2.82,dd(6.0,12.0)	0.00	60.8	60.8	0.0
8				203.2	203.2	0.0
9	5.92,d(16.5)	5.92,d(16.5)	0.00	126.3	126.3	0.0
10	6.25,d(16.5)	6.25,d(16.5)	0.00	155.6	155.5	0.1
11				39.2	39.2	0.0
12	1.56,s	1.56,s	0.00	16.5	16.5	0.0
13a	4.03,dd(7.0,11.5)	4.02,dd(7.0,11.5)	0.01	60.5	60.4	0.1
13b	3.88,dd(5.5,12.0)	3.88,dd(5.5,12.0)	0.00			
14	1.17,s	1.17,s	0.00	23.8	23.8	0.0
15	1.16,s	1.16,s	0.00	28.9	28.9	0.0
16	3.30,s	3.30,s	0.00	57.5	57.5	0.0

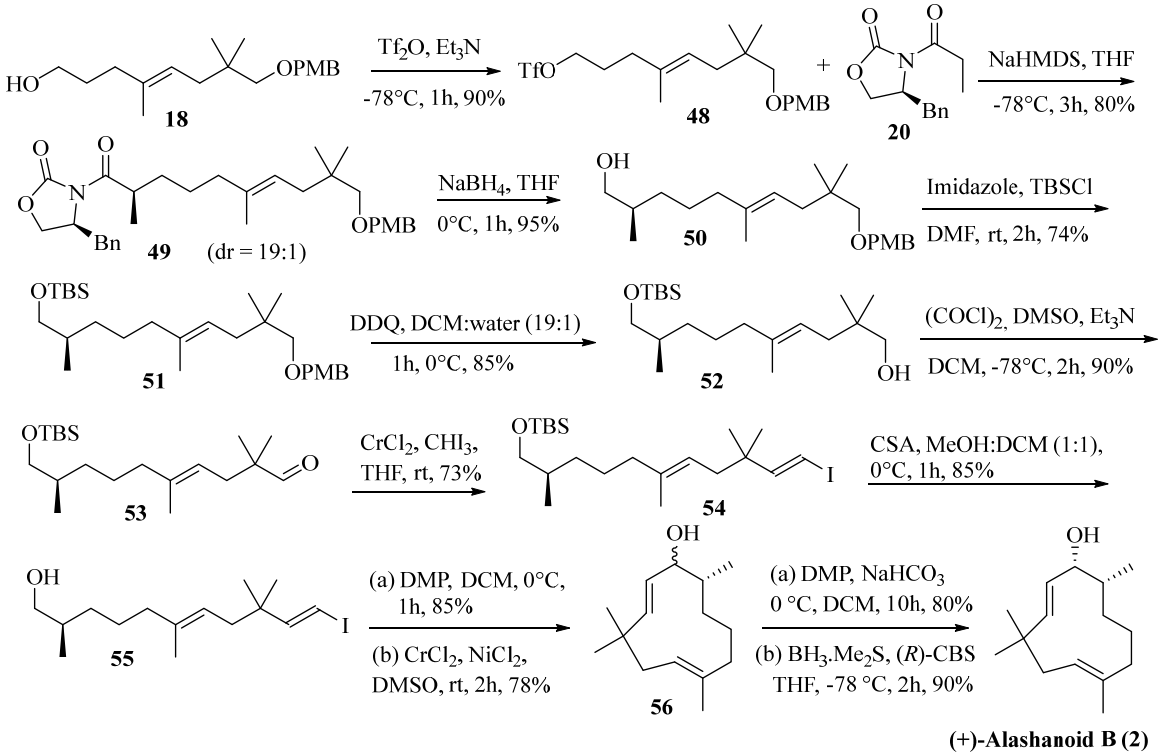
Comparison of ^{1}H NMR spectra of (+)-alashanoid F (7a):



Comparison of ^{13}C NMR spectra of (+)-alashanoid F (7a):

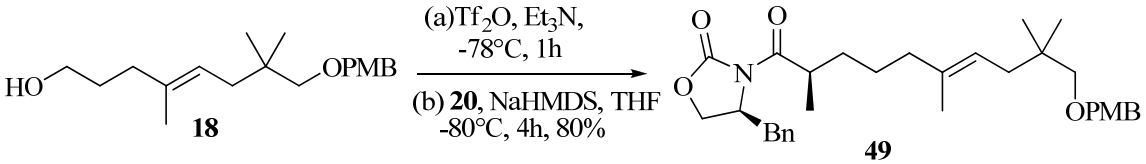


10: Synthesis of alashanoid B:



Scheme S8: Synthesis of **alashanoid B**

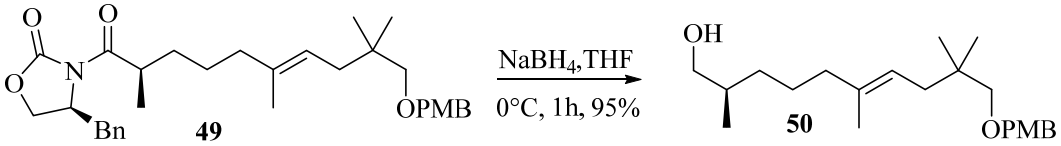
10.1. Synthesis of compound 49:



To a cooled (-78 °C) solution of the alcohol **18** (3.23mmol, 1g) in CH_2Cl_2 (12 mL) was added triethylamine (3.7 mL, 26.1 mmol). After the solution was stirred an additional 5 min at -78 °C, triflic anhydride (2.2 mL, 13 mmol) was added dropwise over a 5 min period, after which the reaction mixture was slowly warmed to -50 °C for an additional 30 min period. The reaction solution was then quenched with $NaHCO_3$, and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo to provide 1.3g (100%) of crude **48**, which was immediately used further as is. To a stirred solution of NaHMDS (10.5 mL 1M in THF, 10.5 mmol, 3.3 eq) in THF (20mL) was added (4*R*)-4-benzyl-3-propionyl-1,3-oxazolidin-2-one (**20**, 2.25g, 9.6 mmol, 3.0 eq) in THF (30 mL) at -80 °C. After 1 h, triflate **48** (1.3 g crude, about 3mmol, 1 eq) in THF (10 mL) was added and the reaction mixture was allowed to warm to -50 °C. After stirring the reaction mixture at this temperature for 4h, the mixture was quenched with saturated NH_4Cl solution (50 mL) and allowed to warm to room temperature. The layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to furnish oxazolidinone **49** (2.34mmol, 1.2 g , 72% over two steps) as a colorless oil. $[\alpha]_D^{25}$= -68.0 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz,$CDCl_3$) δ 7.18 – 7.04 (m, 7H), 6.71 (d, *J* = 8.7 Hz, 2H), 4.99 (t, *J* = 7.2 Hz, 1H), 4.54-4.49 (m, 1H), 4.27 (s, 2H), 4.04 – 3.97 (m, 2H), 3.64 (s,

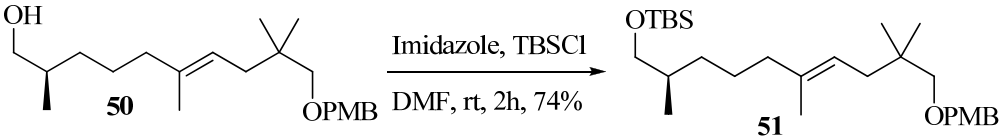
3H), 3.58-3.54 (m, 1H), 3.13-3.09 (m, 1H), 2.94 (s, 2H), 2.63 – 2.59 (m, 1H), 1.88-1.80 (m, 4H), 1.58 – 1.51 (m, 1H), 1.41 (s, 3H), 1.29 – 1.20 (m, 3H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.72 (s, 6H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 177.2, 158.9, 153.0, 136.2, 135.3, 131.2, 129.4, 128.9, 128.8, 127.3, 121.2, 113.6, 78.8, 72.8, 66.0, 55.3, 55.2, 3.9, 37.9, 37.5, 37.1, 35.7, 33.0, 25.5, 24.5, 24.5, 17.3, 15.9. **IR**: 2954, 2926, 2854, 1778, 1698, 1612, 1512, 1456, 1384, 1350, 1244, 1210, 1094, 1034, 970, 822, 750, 702, 506cm^{-1}. **HRMS (ESI) m/z**: for $C_{32}H_{44}NO_5$ $[M + H]^+$, calculated: 522.3219; found: 522.3216.

10.2. Synthesis of compound 50:



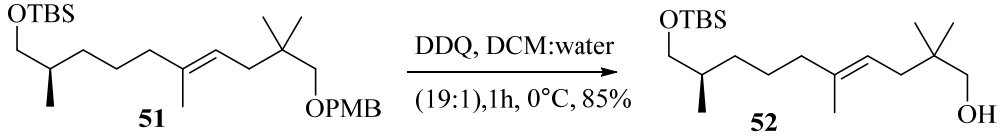
The title compound **50** (2.2 mmol, 775mg, 95% yield) was synthesized from **49** (2.34 mmol, 1.2g) by employing the general method as described earlier (**GPVIB**). $[\alpha]_D^{25}$= +17.4 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 5.07 (t, *J* = 7.2 Hz, 1H), 4.35 (s, 2H), 3.73 (s, 3H), 3.44-3.41 (m, 1H), 3.35 – 3.31 (m, 1H), 3.02 (s, 2H), 1.90 (d, *J* = 7.5 Hz, 4H), 1.61 – 1.50(m, 5H), 1.42 – 1.25 (m, 3H), 1.04 – 0.97 (m, 1H), 0.84 (d, *J* = 6.7 Hz, 3H), 0.81 (s, 6H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 158.9, 136.6, 131.2, 128.8, 120.9, 113.6, 78.8, 72.9, 68.3, 55.2, 40.2, 37.1, 35.7, 35.6, 32.7, 25.3, 24.5, 16.6, 15.9. **IR**: 3388, 2954, 2922, 2852, 1614, 1514, 1464, 1378, 1362, 1302, 1248, 1172, 1094, 1038, 822cm^{-1}. **HRMS(ESI) m/z**: for $C_{22}H_{37}O_3$ $[M + H]^+$, calculated: 349.2743; found: 349.2745.

10.3. Synthesis of compound 51:



Compound **51** (1.66 mmol, 770mg, 74% yield) was synthesized from **50** (2.2 mmol, 775mg) by employing the general method as described earlier (**GPVII**). $[\alpha]_D^{25}$= +7.7(c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 6.3 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.11 (t, *J* = 7.2 Hz, 1H), 4.39 (s, 2H), 3.77 (s, 3H), 3.43-3.40 (m, 1H), 3.33-3.30 (m, 1H), 3.06 (s, 2H), 1.93 (d, *J* = 7.6 Hz, 4H), 1.52 (d, *J* = 15.8 Hz, 4H), 1.45 – 1.27 (m, 3H), 1.08-0.97 (m, 1H), 0.86 – 0.83 (m, 18H), -0.00 (s, 6H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 158.9, 136.8, 131.2, 128.8, 120.8, 113.6, 78.8, 72.9, 68.4, 55.2, 40.3, 37.1, 35.7, 35.6, 32.9, 25.9, 25.4, 24.5, 18.3, 16.7, 15.9, -5.3. **IR:** 2952,2926,2854,1612,1514,1462,1360,1248,1172, 1096,1040, 836,774 cm^{-1}. **HRMS (ESI) m/z**: for $C_{28}H_{51}O_3Si$ $[M + H]^+$, calculated: 463.3607; found: 463.3603.

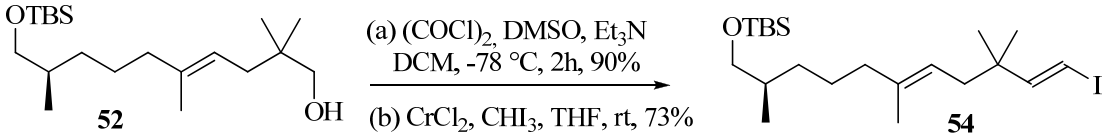
10.4 Synthesis of compound 52:



Compound **52** (1.41 mmol, 480mg, 85% yield) was synthesized from **51** (1.66 mmol, 770mg) by employing the general method as described earlier (**GPVIII**). $[\alpha]_D^{25}$= +19.0 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.17 (t, *J* = 8.3 Hz, 1H), 3.42-3.39 (m, 1H), 3.37-3.31 (m, 1H), 3.29 (s, 2H), 1.97 – 1.91 (m, 4H), 1.57 – 1.52 (m, 4H), 1.44 – 1.28 (m, 3H), 1.04 – 0.95(m, 1H), 0.86-0.83 (m, 18H), -0.00 (s,

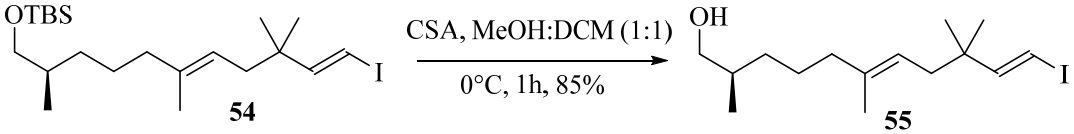
6H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 137.3, 120.4, 72.0, 68.4, 40.3, 36.9, 36.3, 35.6, 32.8, 25.9, 25.4, 23.8, 18.3, 16.7, 16.0, -5.3. **IR**: 3342, 2954, 2924, 2856, 1726, 1462, 1382, 1256, 1042, 836, 776cm^{-1}. **HRMS (ESI) m/z**: for $C_{20}H_{42}O_2Si$ $[M + H]^+$, calculated: 343.3032; found: 343.3029.

10.5. Synthesis of compound 54:



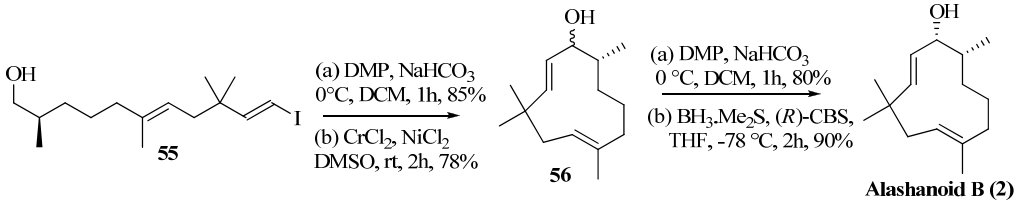
Compound (*E*)-**54** (0.92 mmol, 430mg, 66% over 2 steps) was synthesized from **52** (1.41 mmol, 480mg) by employing the general method as described earlier (**GP1** and **GPXI**). $[\alpha]_D^{25}$= +23.0 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.48 (d, *J* = 14.6 Hz, 1H), 5.87 (d, *J* = 14.6 Hz, 1H), 5.06 (t, *J* = 7.1 Hz, 1H), 3.43-3.40 (m, 1H), 3.34-3.31 (m, 1H), 1.94 (d, *J* = 7.4 Hz, 4H), 1.55 – 1.50 (m, 5H), 1.42 – 1.27 (m, 3H), 1.10 – 0.97 (m, 2H), 0.95 (s, 6H), 0.86 – 0.83 (m, 12H), -0.00 (s, 6H).**^{13}C NMR {^{1}H}** (125 MHz, $CDCl_3$) δ 155.8, 137.7, 119.9, 72.2, 68.4, 41.6, 40.3, 40.2, 35.7, 32.8, 26.1, 26.0, 25.9, 25.4, 18.3, 16.7, 16.0, -5.3. **IR**: 2958,2920,2850,1462,1034,952cm^{-1}. **HRMS (ESI) m/z**: for $C_{21}H_{41}IKOSi$ $[M + K]^+$, calculated: 503.1608; found: 503.1648.

10.6. Synthesis of compound 55:



Compound (*E*)-**55** (0.78 mmol, 274mg, 85% yield) was synthesized from **54** (0.92 mmol, 430mg) by employing the general method as described earlier (**GPIX**). $[\alpha]_D^{25}$= +39.4 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.41 (d, *J* = 14.6 Hz, 1H), 5.81 (d, *J* = 14.6 Hz, 1H), 5.00 (t, *J* = 7.1 Hz, 1H), 3.44-3.40 (m, 1H), 3.35-3.31 (m, 1H), 1.89 (t, *J* = 10.9 Hz, 4H), 1.60 – 1.49 (m, 1H), 1.47 (s, 3H), 1.37 – 1.32 (m, 2H), 1.32 – 1.23 (m, 2H), 1.04 – 0.94 (m, 1H), 0.89 (s, 6H), 0.83 (d, *J* = 6.7 Hz, 3H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 155.7, 137.5, 120.1, 72.2, 68.3, 41.6, 40.2, 40.1, 35.7, 32.6, 26.1, 25.3, 16.6, 16.0.**IR**: 3352, 2956, 2920, 2850, 1462, 1384, 1032, 952cm^{-1}. **HRMS (ESI) m/z**: for $C_{15}H_{31}INO$ $[M + NH_4]^+$, calculated: 368.1436; found: 368.1450.

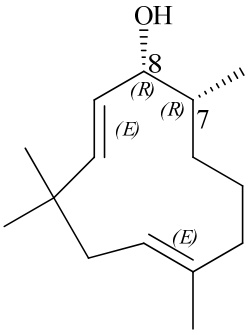
10.7. Synthesis of alashanoid B (2):



Compound **56** (0.5 mmol, 115mg, 66% yield over 2 steps) was synthesized from compound **55** (0.7 mmol, 270mg) by employing the general method as described earlier (**GPX** and **GPXII**). Next DMP oxidation by previously described method (**GPX**) on **56** provided the enone as reduction precursor. To a stirred solution of the enone (60 mg, 0.272 mmol) in THF (2.0 mL) were added (*R*)-CBS catalyst (1 M solution in toluene, 1.36 mL, 1.36 mmol) and $BH_3 \cdot SMe_2$ (2.0 M solution in THF, 0.68 mL, 1.36 mmol) at –78 °C and stirring was continued for 1h. The reaction was quenched by addition of MeOH (0.5 mL), and the resultant mixture was poured into brine (10 mL). The whole was extracted with Et_2O (10 mL × 3).

The combined extracts were dried (Na_2SO_4) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel produce alashanoid B (**2**) as a white solid (0.244mmol, 54 mg, 90% yield). $[\alpha]_D^{25}$= +51.3 (c = 0.1, MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.35 (dd, *J* = 16.0, 6.0 Hz, 1H), 5.17 (d, *J* = 16.5 Hz, 1H), 5.05 (dd, *J* = 8.5,7.0 Hz,1H), 4.13 (d, *J* = 5.0 Hz, 1H), 2.10 (m, 1H), 1.99 (dd, *J* = 12.5, 10.5 Hz, 1H), 1.86 (dd, *J*=3.0,12.0 Hz, 1H),1.81(overlap,1H) ,1.62 (m, 1H), 1.50 (s, 3H), 1.42 (m, 1H), 1.24 ,1.20 (overlap, 2H), 1.10 (s, 3H), 1.08 (s, 3H), 1.04 (m, 1H), 0.99 (d, *J* = 7.0 Hz, 3H).**^{13}C NMR{^{1}H}** (125 MHz, $CDCl_3$) δ 137.4, 134.3, 131.3, 124.9, 76.6, 42.4, 40.9, 40.7, 37.6, 29.1, 26.5,25.1,23.7,17.7,16.2. **IR**: 3422, 2929. 2858, 1687, 1516, 1451, 1385, 1364, 1270, 1254, 1215, 1180, 1165, 1103, 1079, 1058, 997, 971, 751, 719, 697, 668 cm^{-1}.

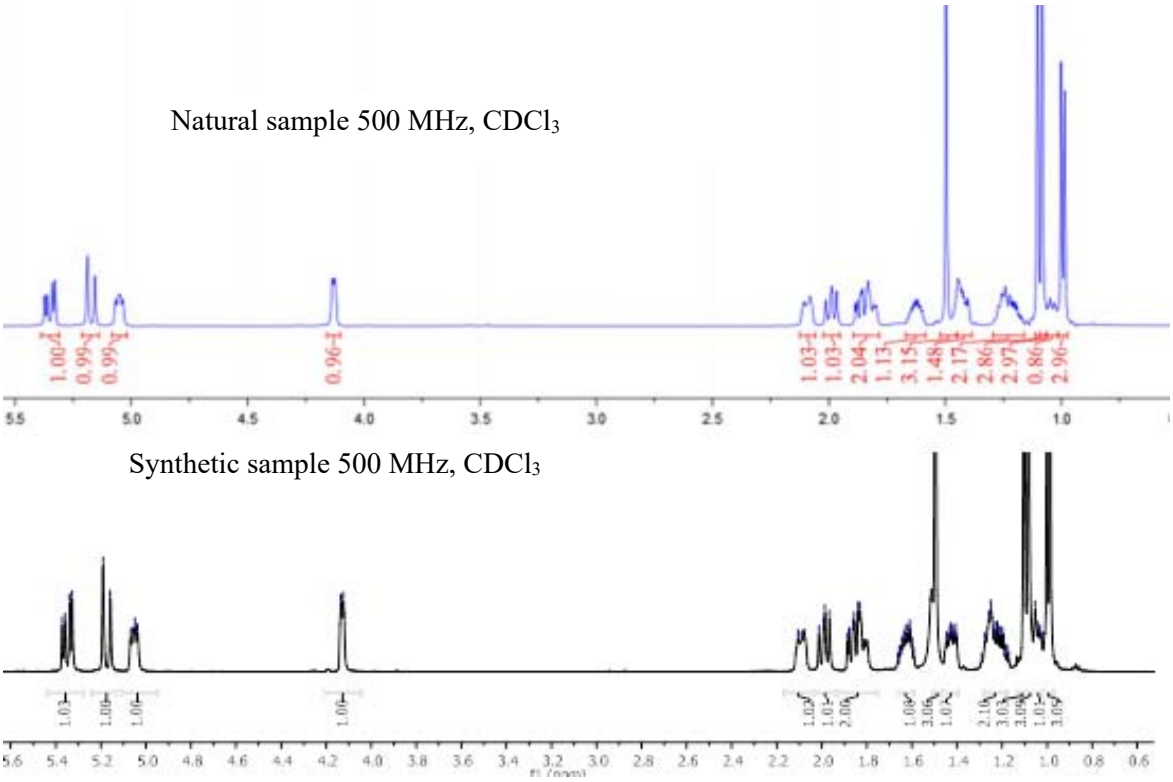
NMR comparison data of natural and synthetic alashanoid B (2)



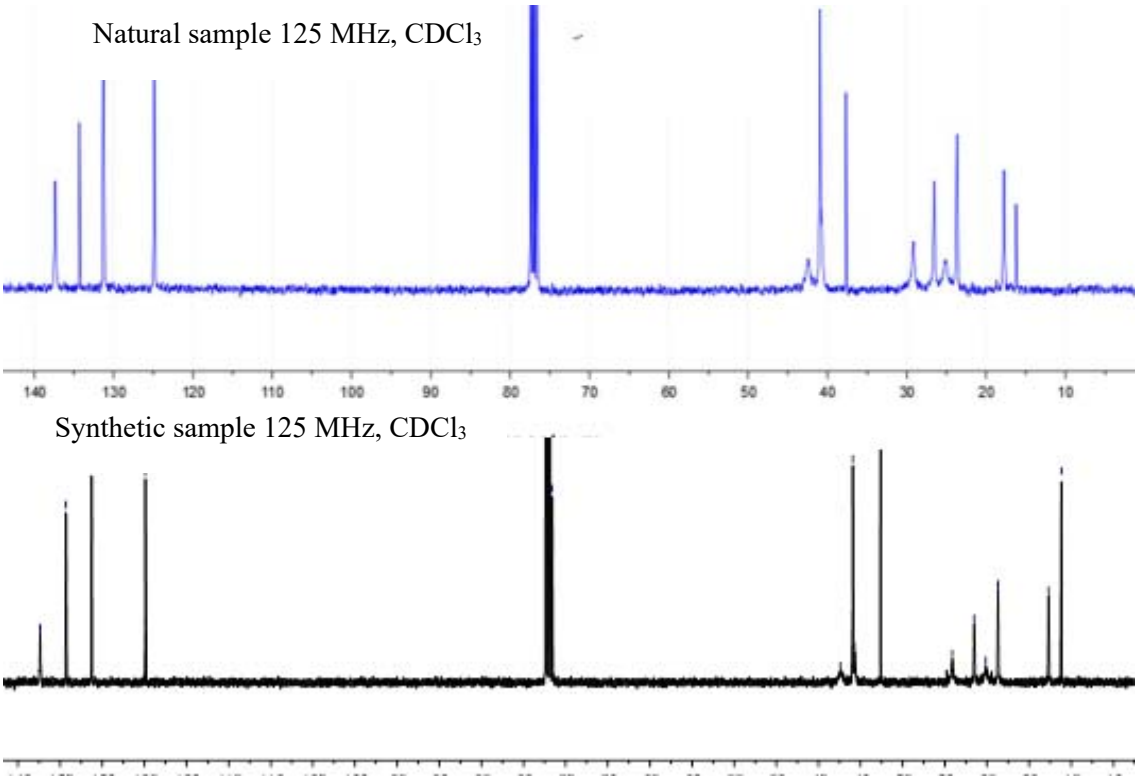
Alashanoid B (2)

Position	Reported ^{1}H δ (ppm); *J* (Hz)	Observed ^{1}H δ (ppm); *J* (Hz)	Δδ (ppm)	Reported ^{13}C δ (ppm)	Observed ^{13}C δ (ppm)	Δδ (ppm)
1a	1.99,dd(10.5,12.5)	1.99,dd(10.5,12.5)	0.00	40.8	40.7	0.1
1b	1.81,overlap	1.81,overlap	0.00			
2	5.05,dd(7.0,8.5)	5.05,dd(7.0,8.5)	0.00	124.9	124.9	0.0
3				134.3	134.3	0.0
4a	2.10,m	2.10,m	0.00	40.9	40.9	0.0
4b	1.86,dd(3.0,12.0)	1.86,dd(3.0,12.0)	0.00			
5a	1.20,overlap	1.20,overlap	0.00	23.7	23.7	0.0
5b	1.62,m	1.62,m	0.00			
6a	1.04,m	1.04,m	0.00	26.5	26.5	0.0
6b	1.42,m	1.42,m	0.00			
7	1.24,overlap	1.24,overlap	0.00	42.4	42.4	0.0
8	4.13,d(5.0)	4.13,d(5.0)	0.00	76.6	76.6	0.0
9	5.35,dd(6.0,16.0)	5.35,dd(6.0,16.0)	0.00	131.3	131.3	0.0
10	5.17,d(16.5)	5.17,d(16.5)	0.00	137.4	137.4	0.0
11				37.6	37.6	0.0
12	1.50,s	1.50,s	0.00	16.2	16.2	0.0
13	0.99,d(7.0)	0.99,d(7.0)	0.00	17.7	17.7	0.0
14	1.10,s	1.10,s	0.00	25.1	25.1	0.0
15	1.08,s	1.08,s	0.00	29.2	29.1	0.1

Comparison of ^{1}H NMR spectra of alashanoid B (2):

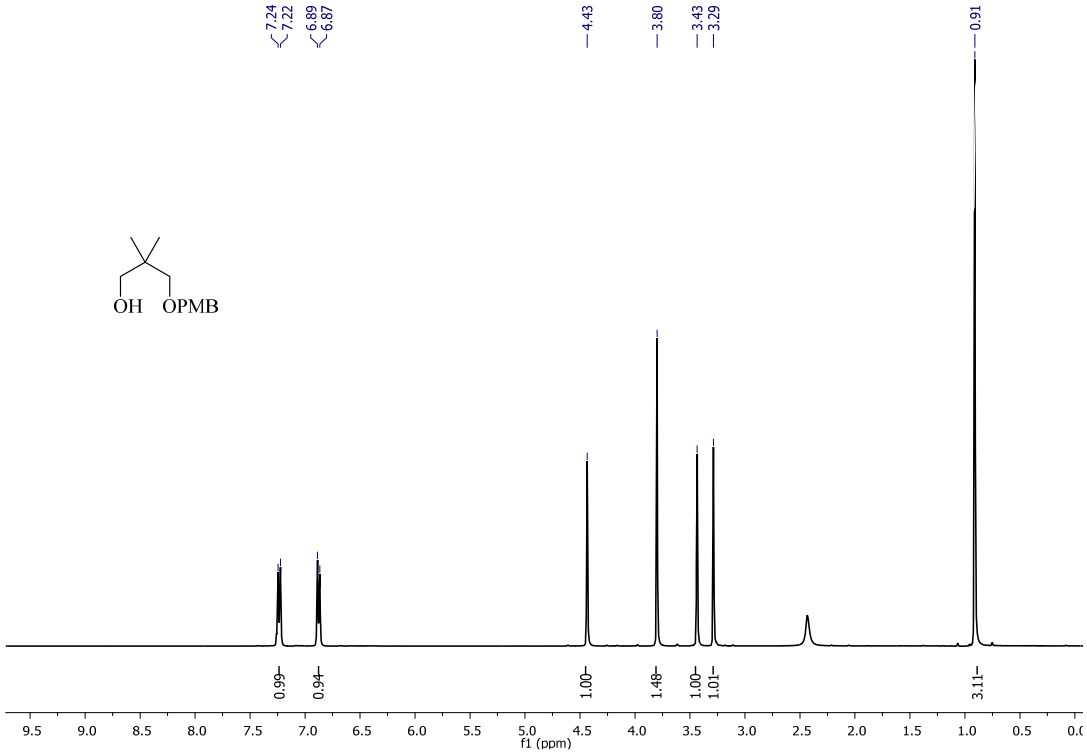


Comparison of ^{13}C NMR spectra of alashanoid B (2):

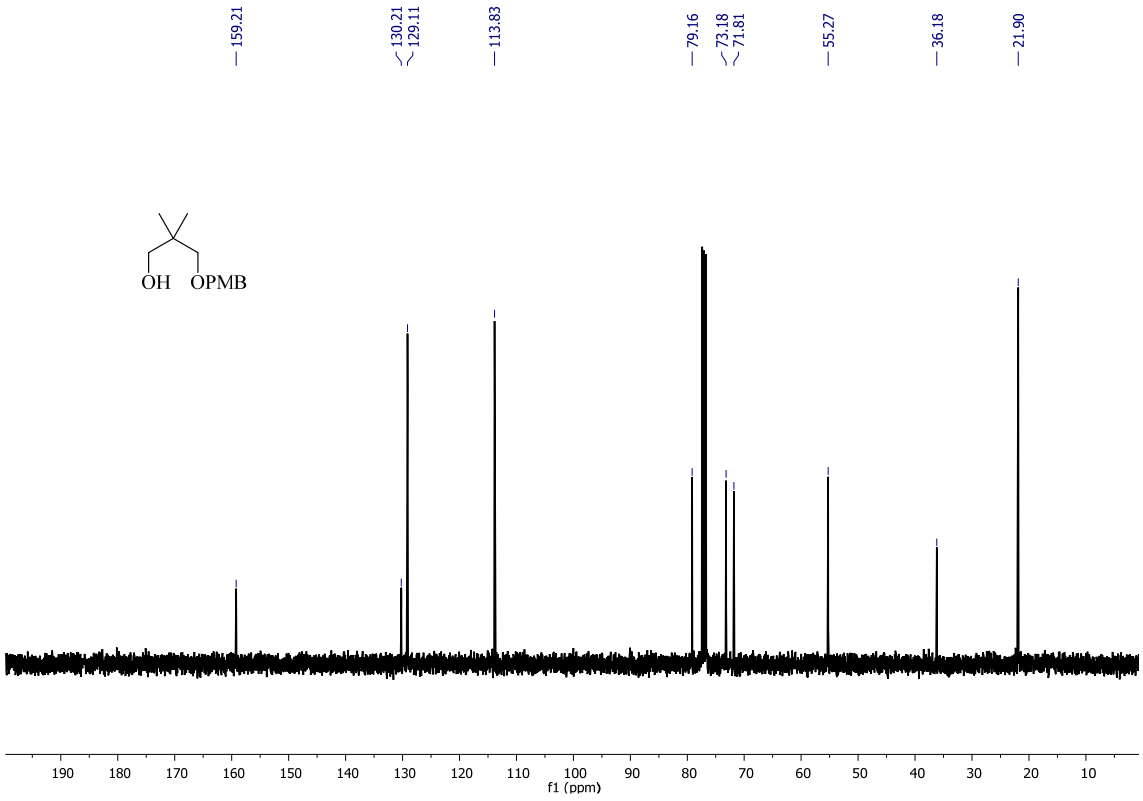


11. Copies of ^{1}H and ^{13}C NMR spectra of the synthesized compounds:

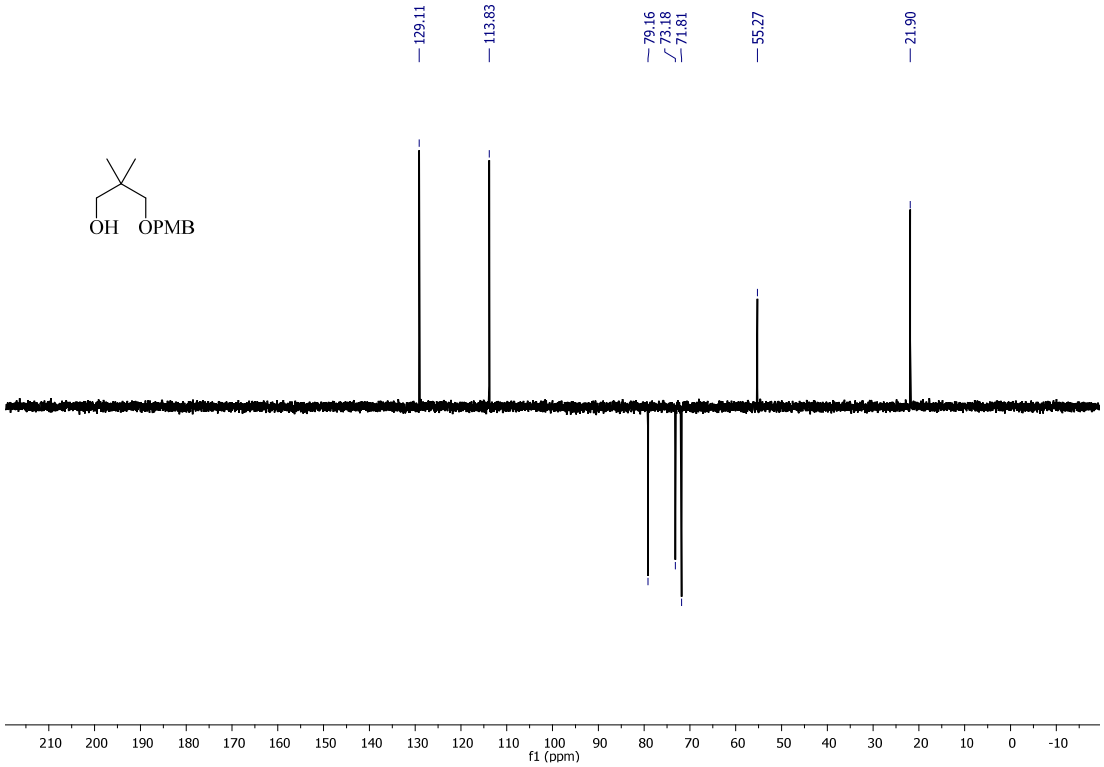
^{1}H NMR of compound 9 (400 MHz, $CDCl_3$)



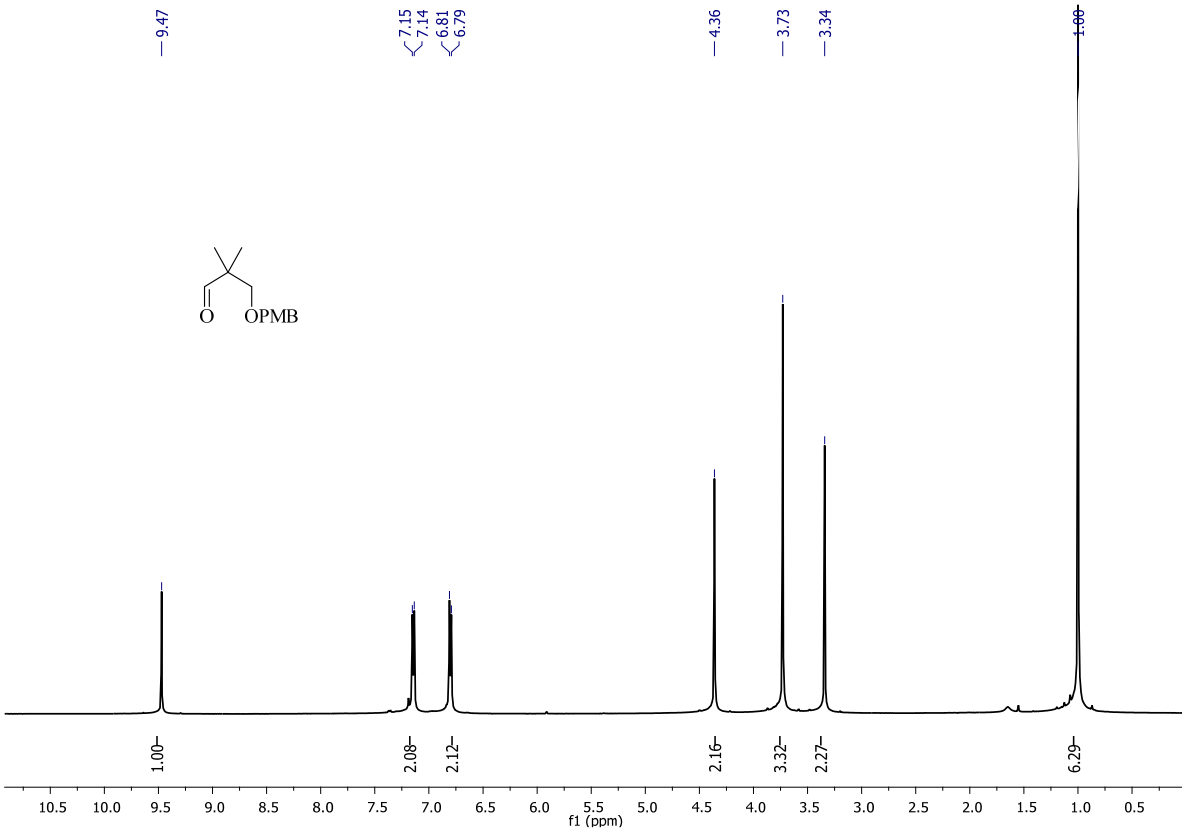
^{13}C NMR of compound 9 (100 MHz, $CDCl_3$)



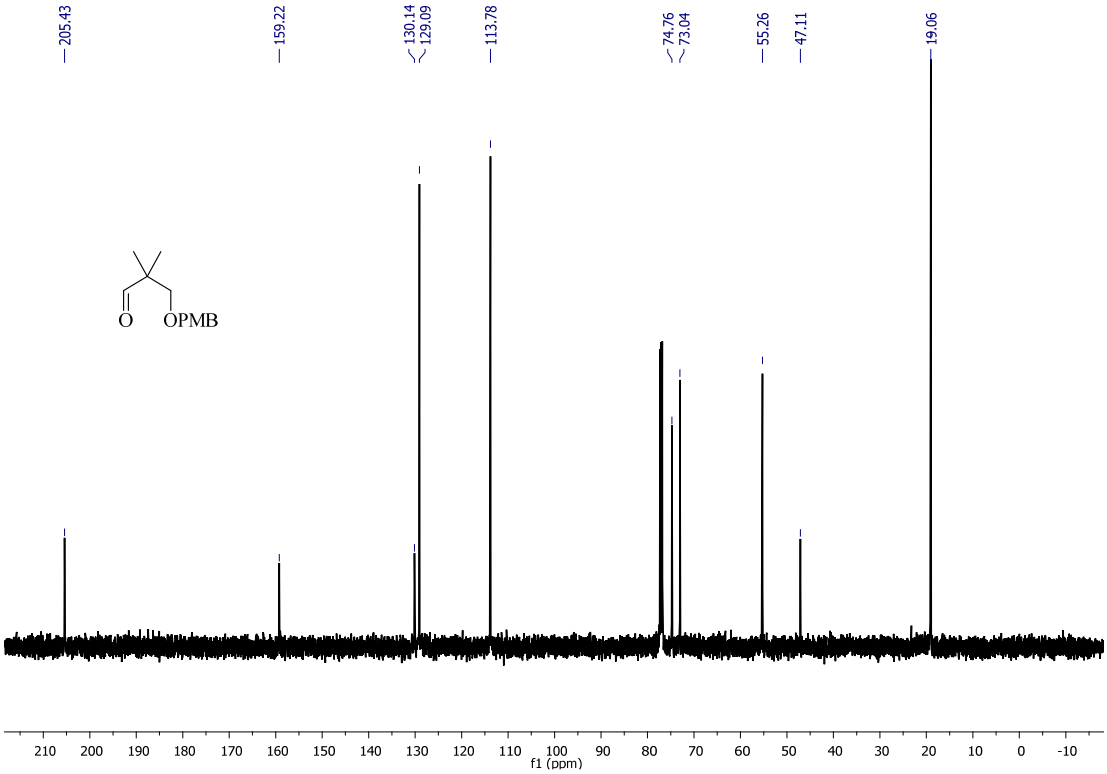
DEPT-135 of compound 9 (100 MHz, $CDCl_3$)



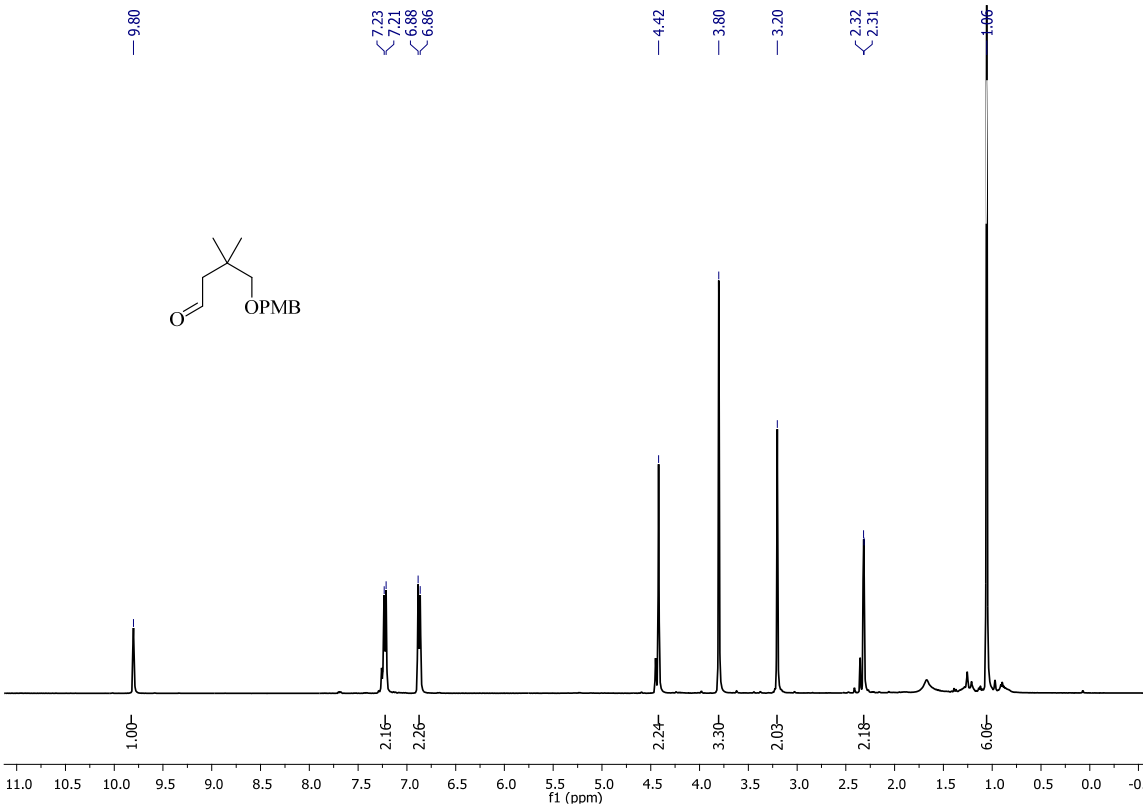
^{1}H NMR of compound 10 (500 MHz, $CDCl_3$)



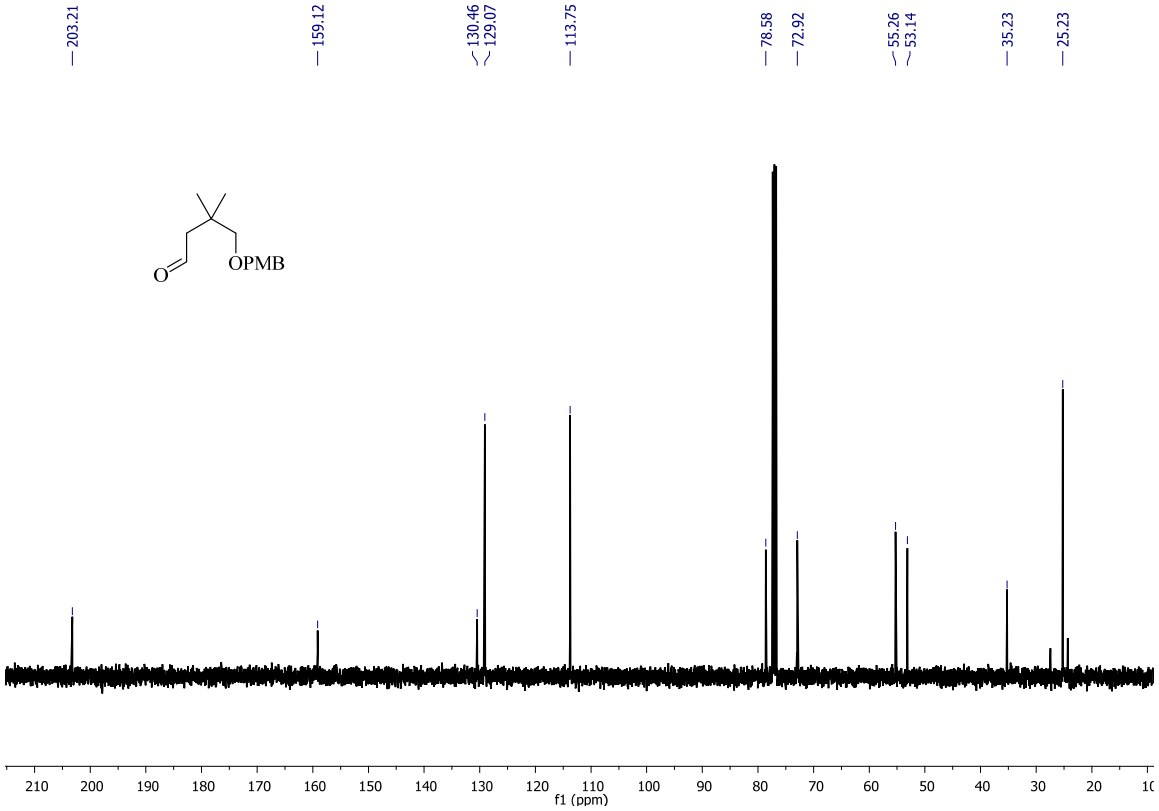
^{13}C NMR of compound 10 (125MHz, $CDCl_3$)



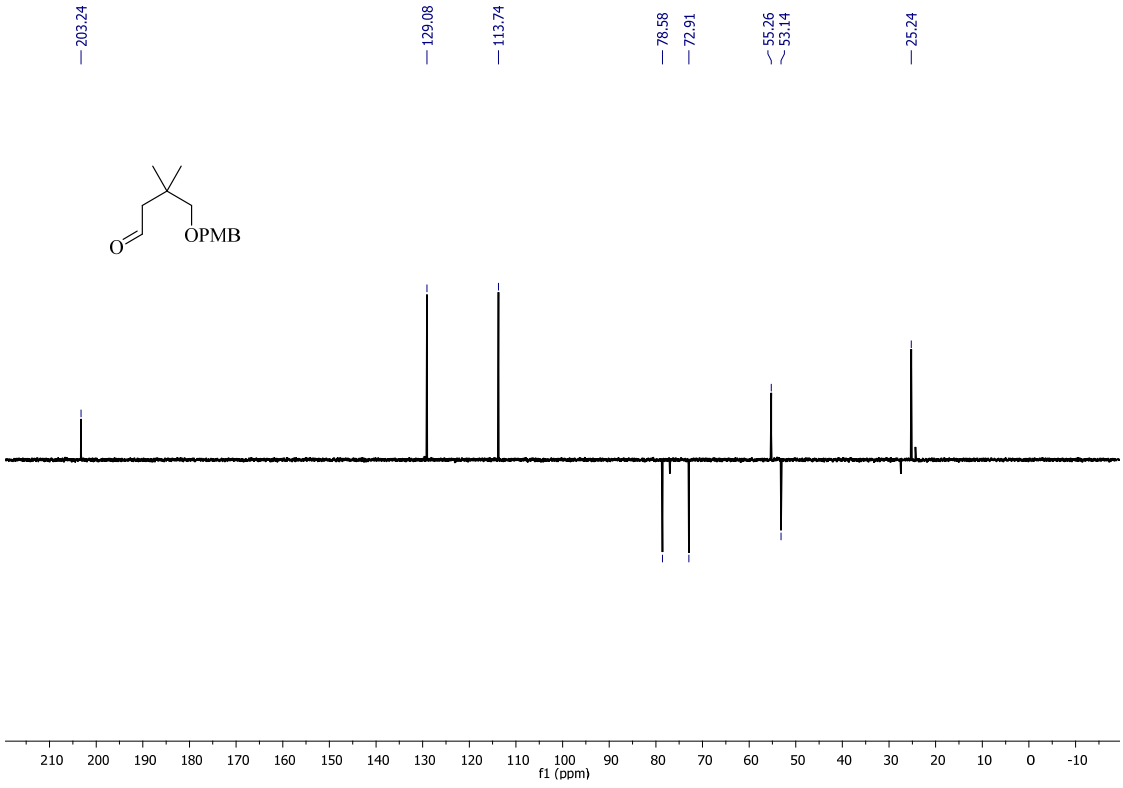
^{1}H NMR of compound 11 (400 MHz, $CDCl_3$)



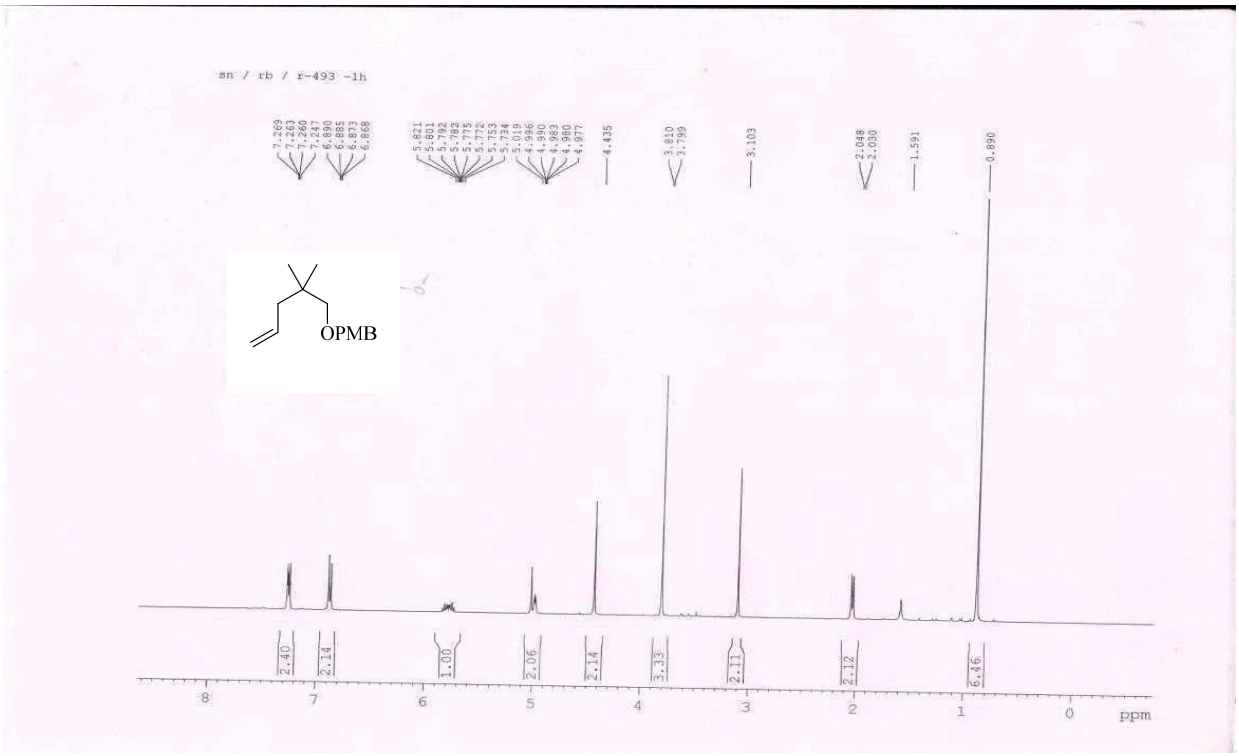
^{13}C NMR of compound 11 (100 MHz, $CDCl_3$)



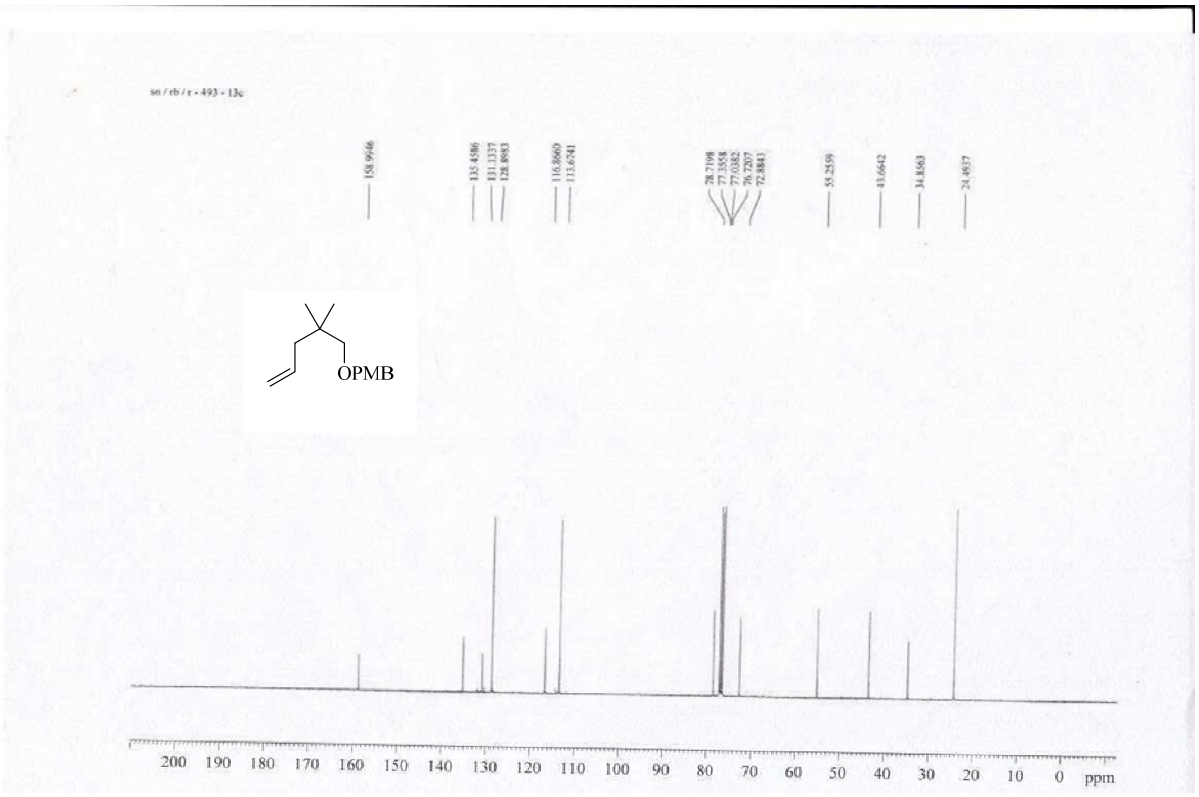
DEPT-135 of compound 11 (100 MHz, $CDCl_3$)



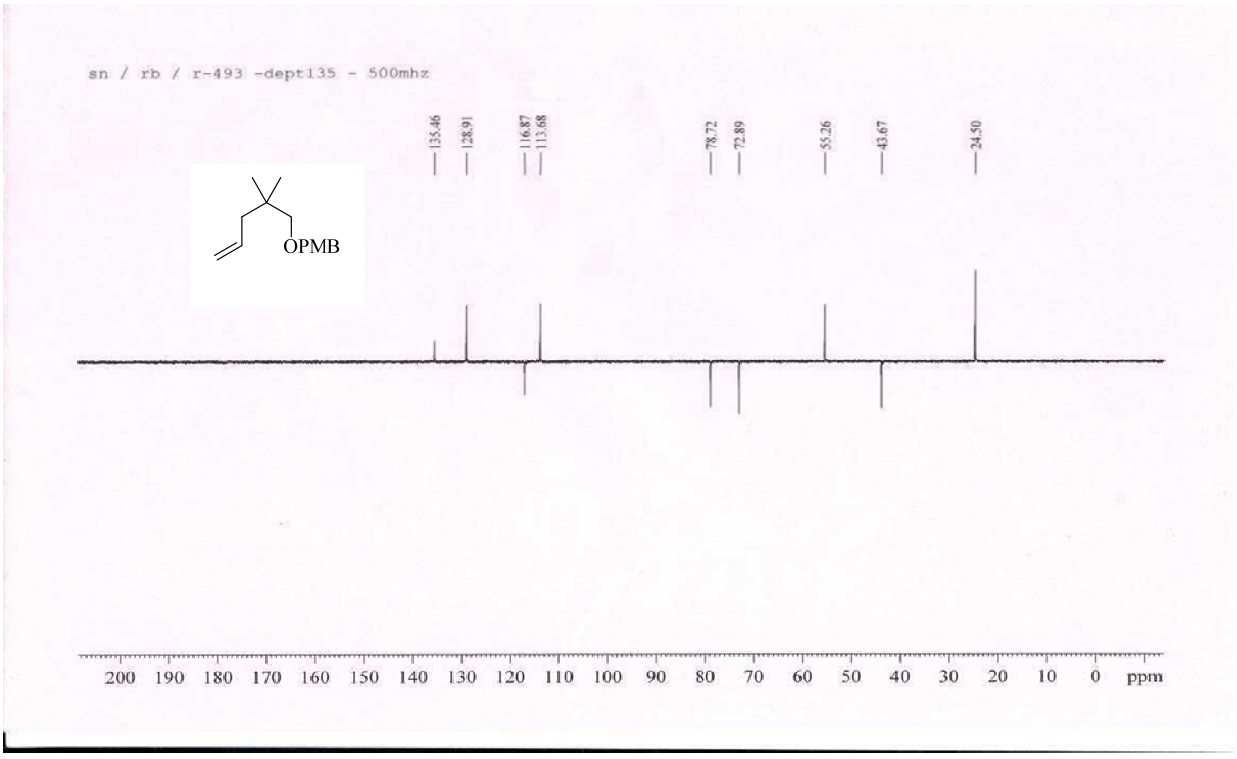
^{1}H NMR of compound 12 (400 MHz, $CDCl_3$)



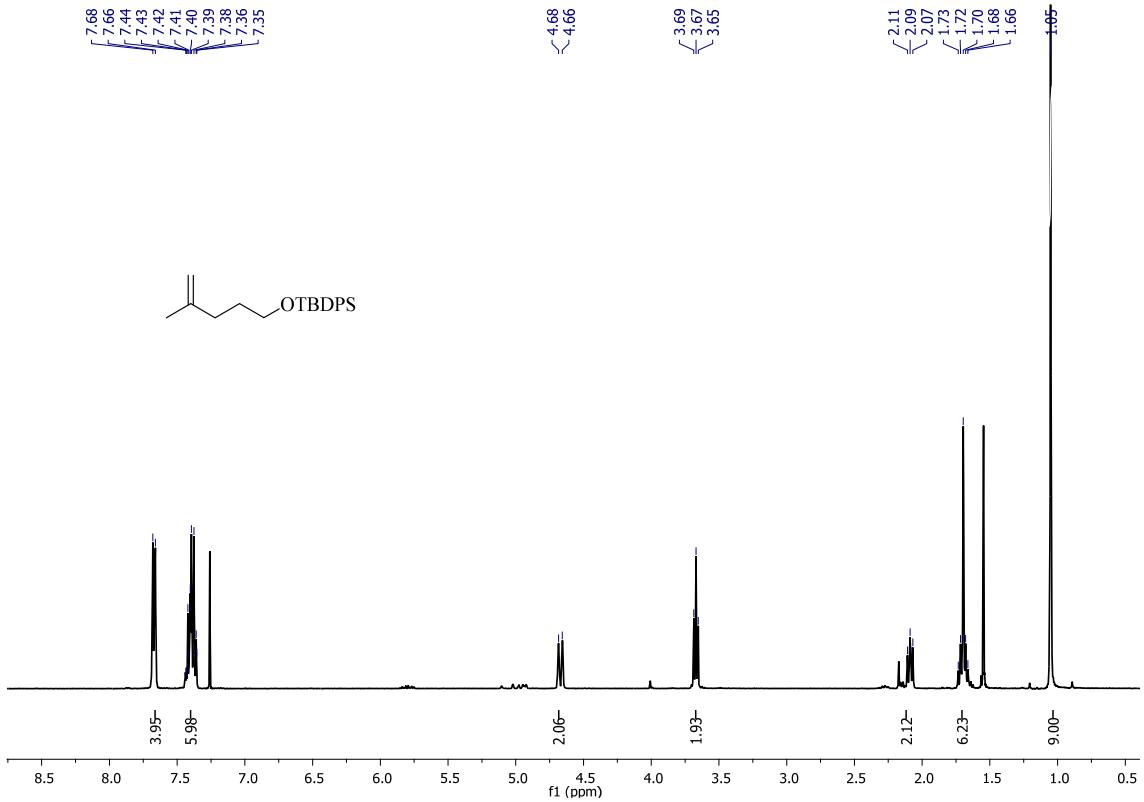
^{13}C NMR of compound 12 (100 MHz, $CDCl_3$)



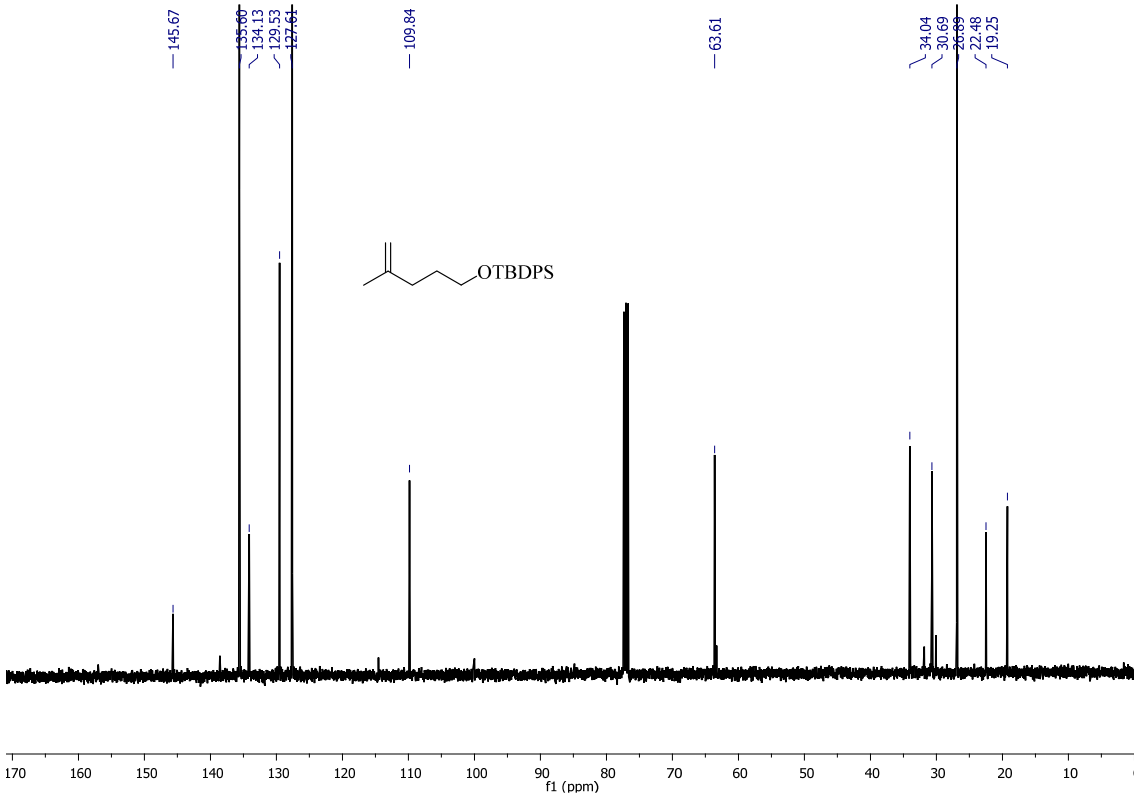
DEPT-135 of compound 12 (100 MHz, $CDCl_3$)



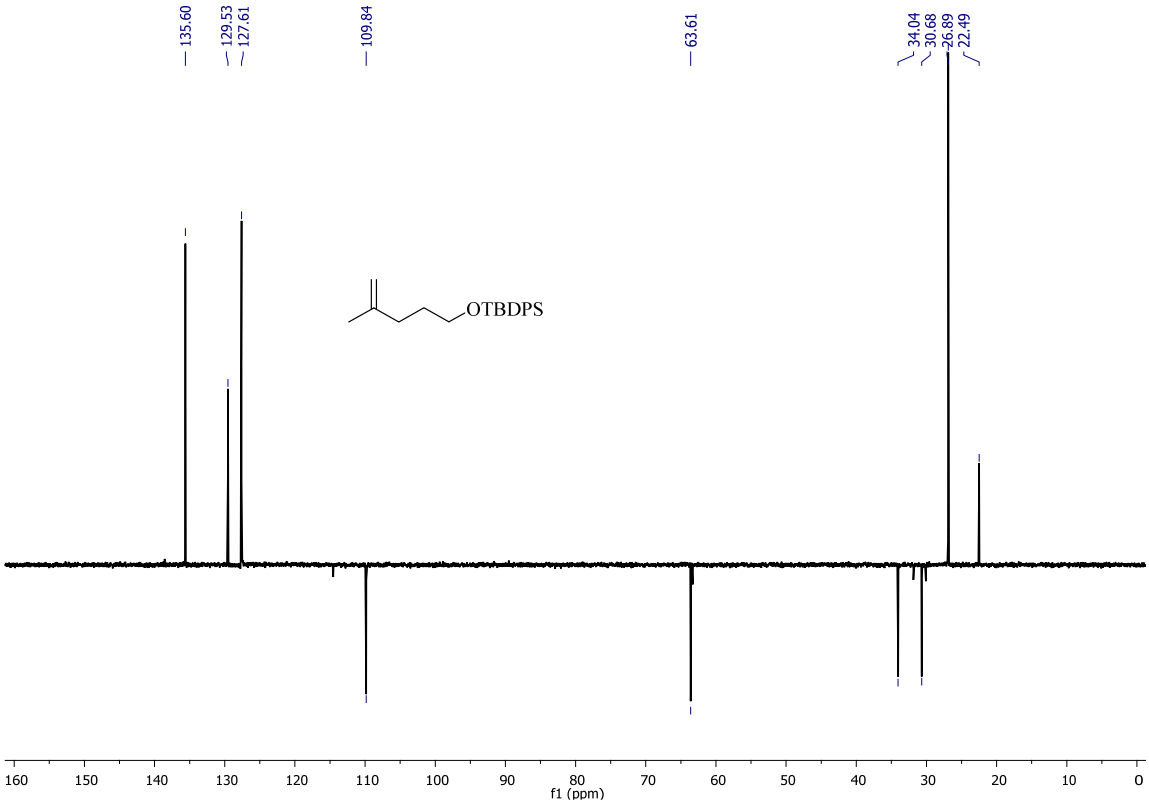
^{1}H NMR of compound 15 (400 MHz, $CDCl_3$)



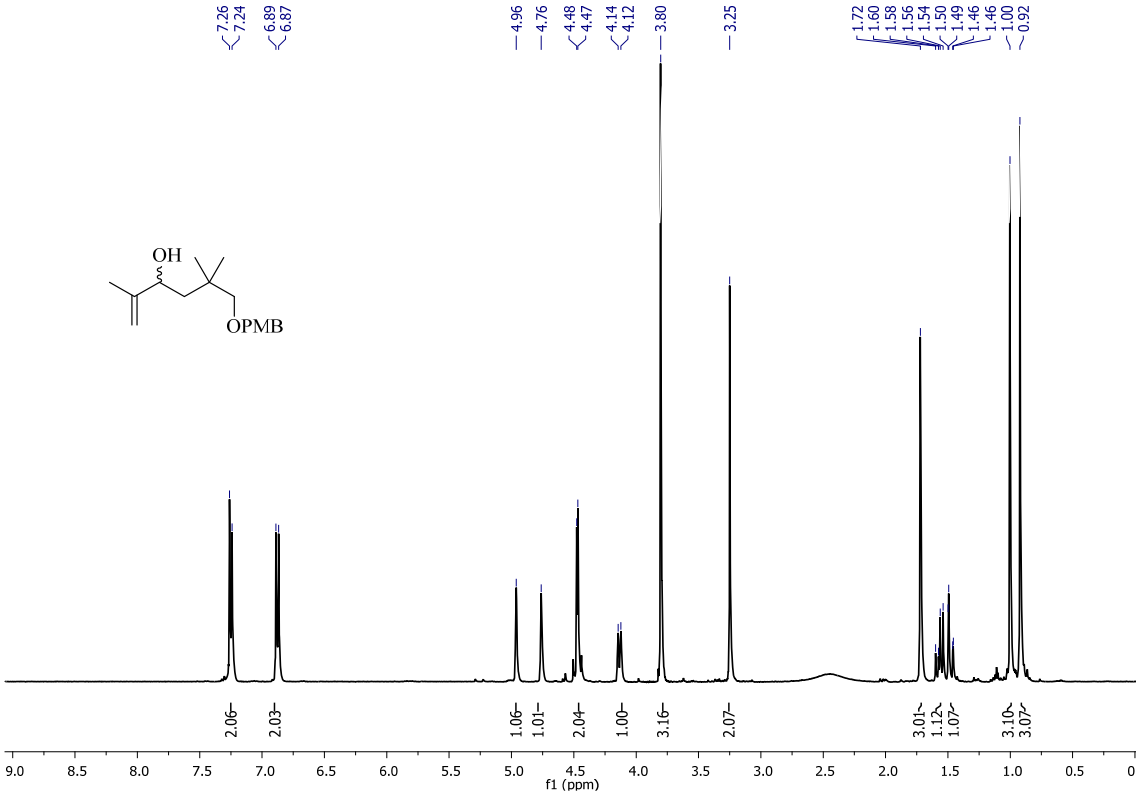
^{13}C NMR of compound 15 (100 MHz, $CDCl_3$)



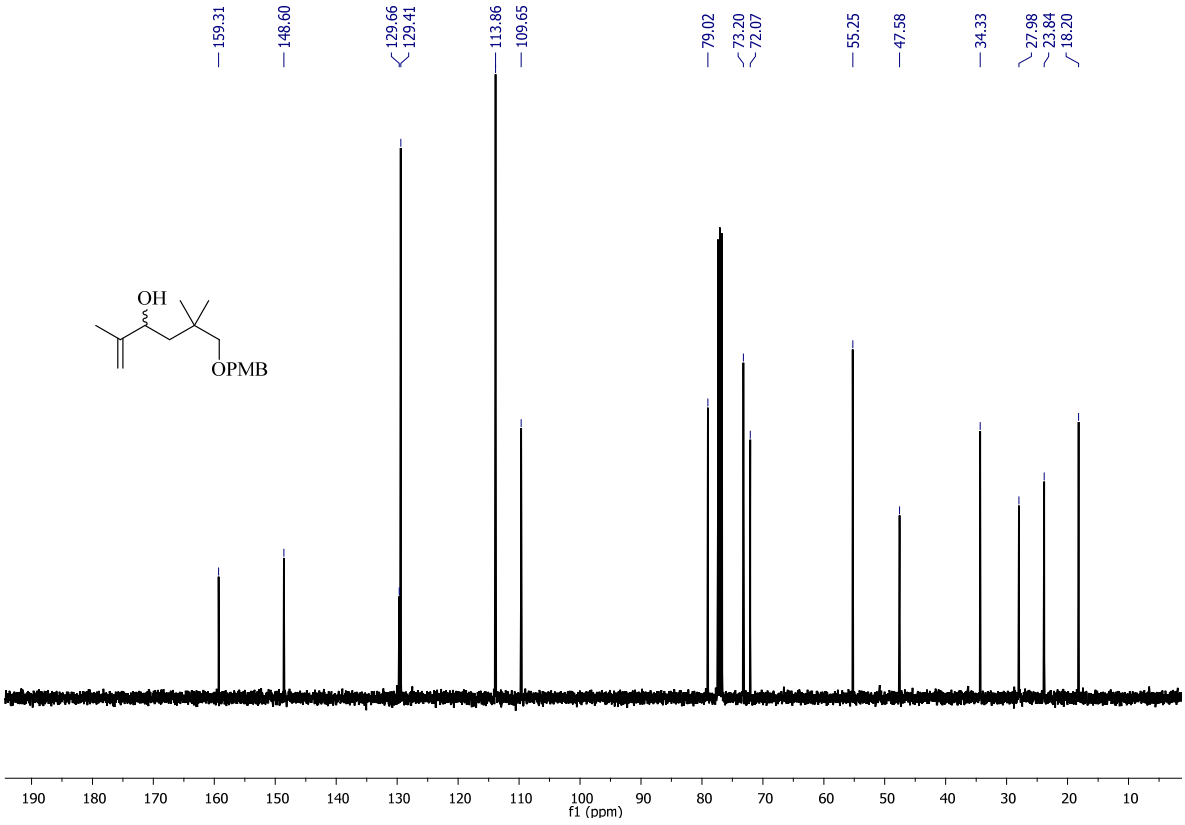
DEPT-135 of compound 15 (100 MHz, $CDCl_3$)



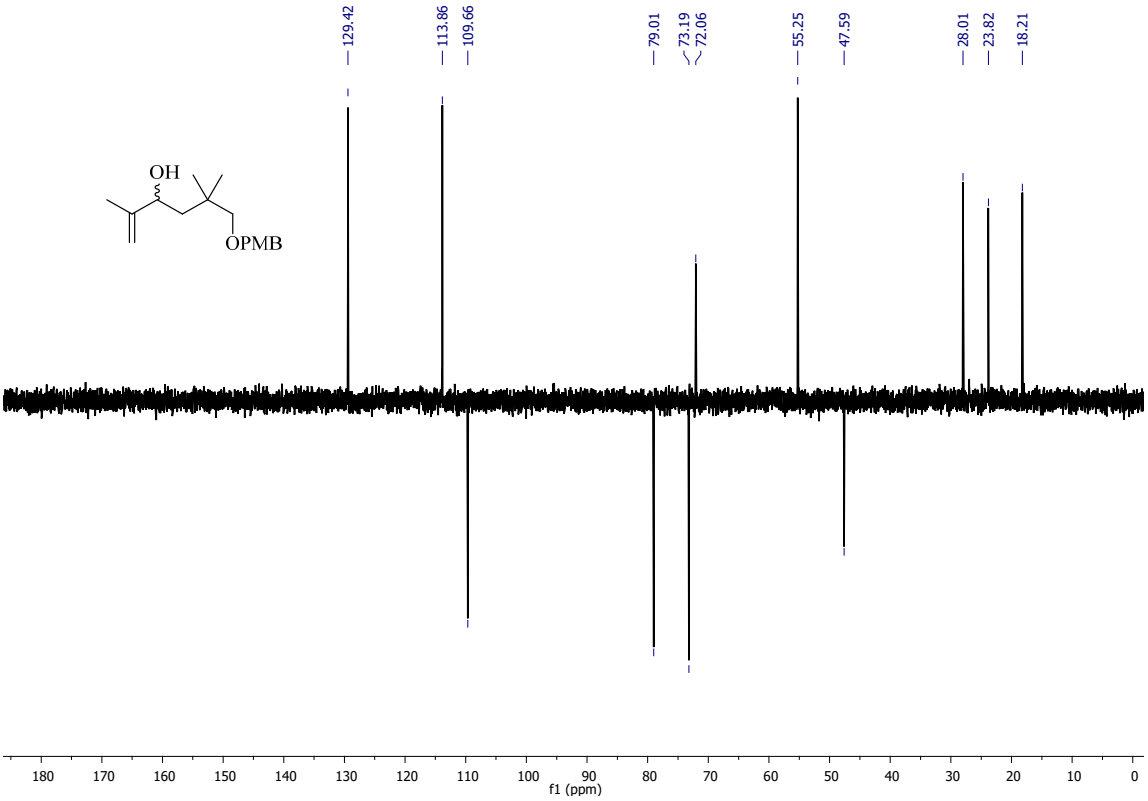
^{1}H NMR of compound 16 (400 MHz, $CDCl_3$)



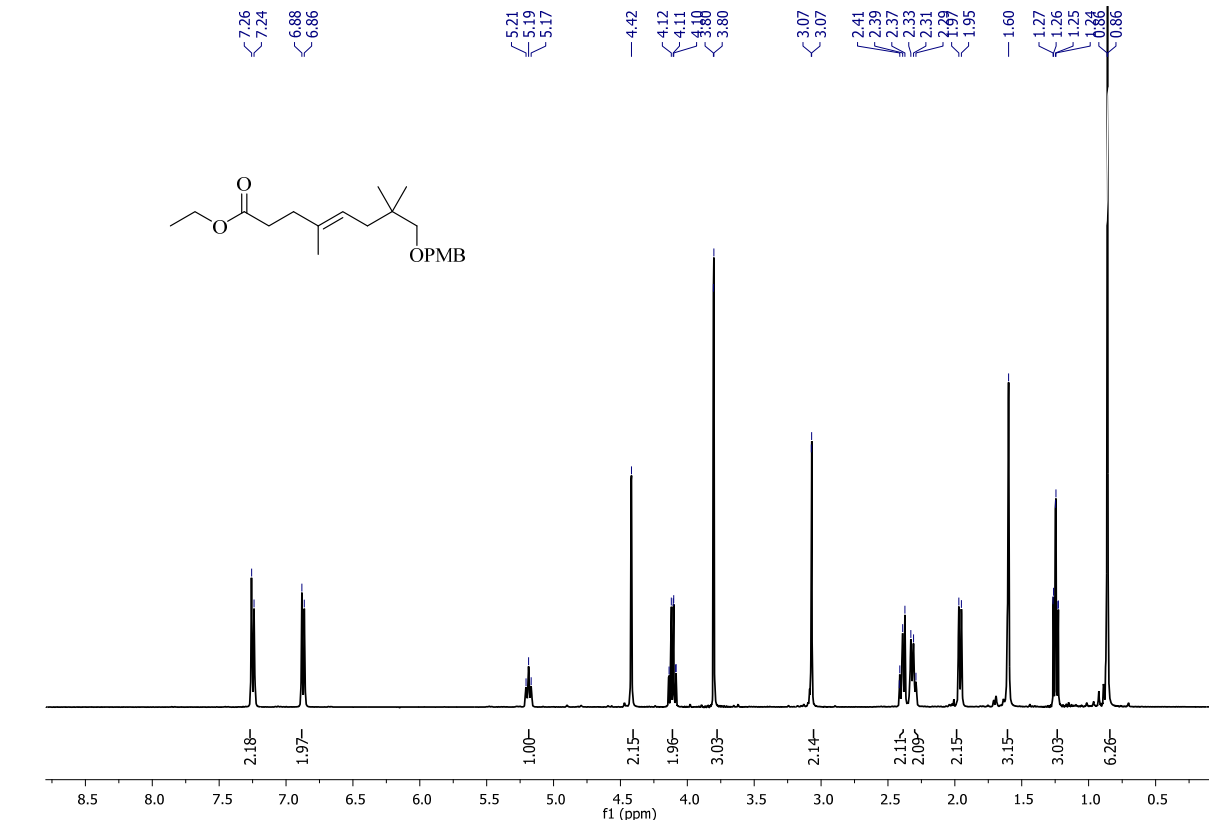
^{13}C NMR of compound 16 (100 MHz, $CDCl_3$)



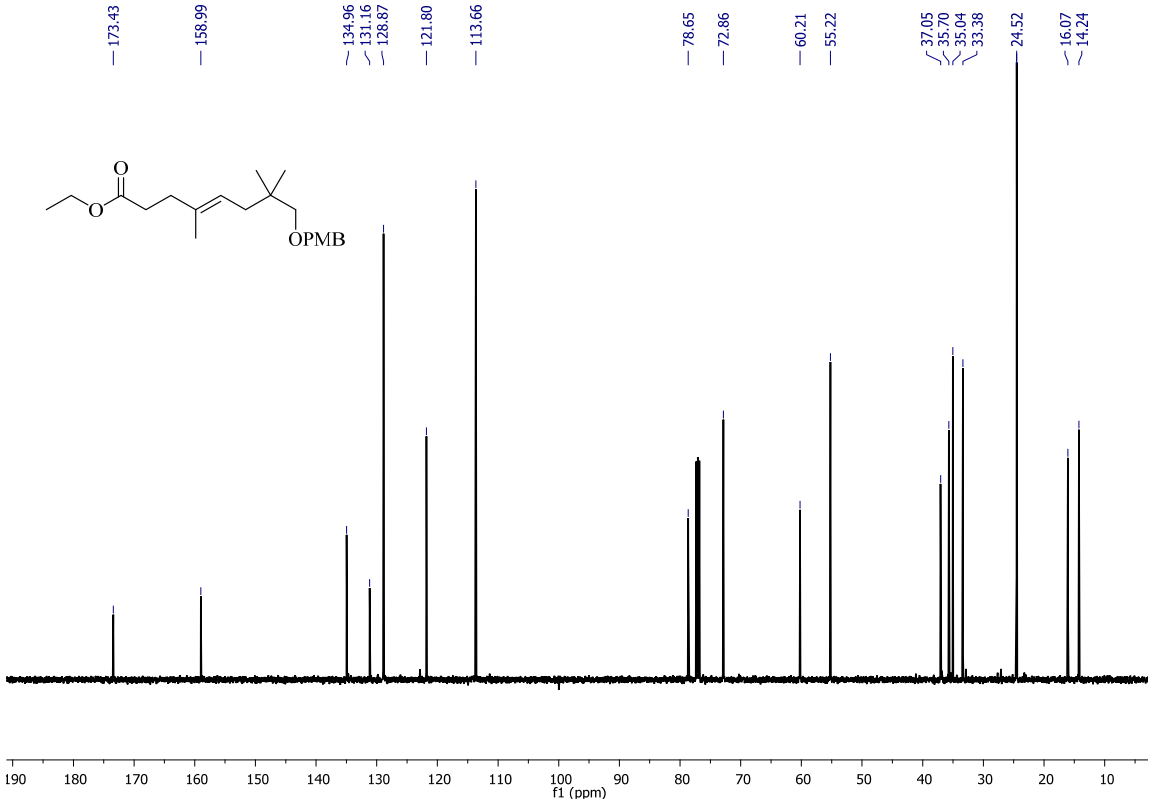
DEPT-135 of compound 16 (100 MHz, $CDCl_3$)



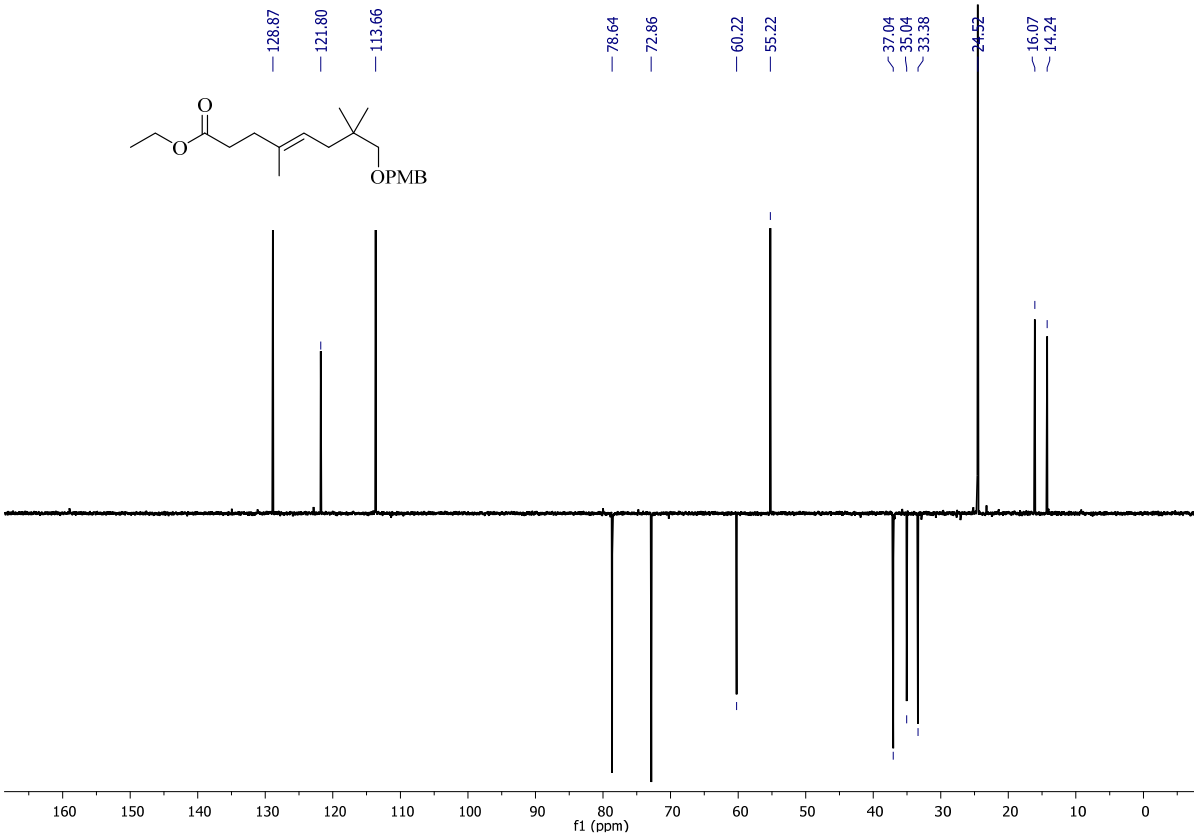
^{1}H NMR of compound 17 (500 MHz, $CDCl_3$)



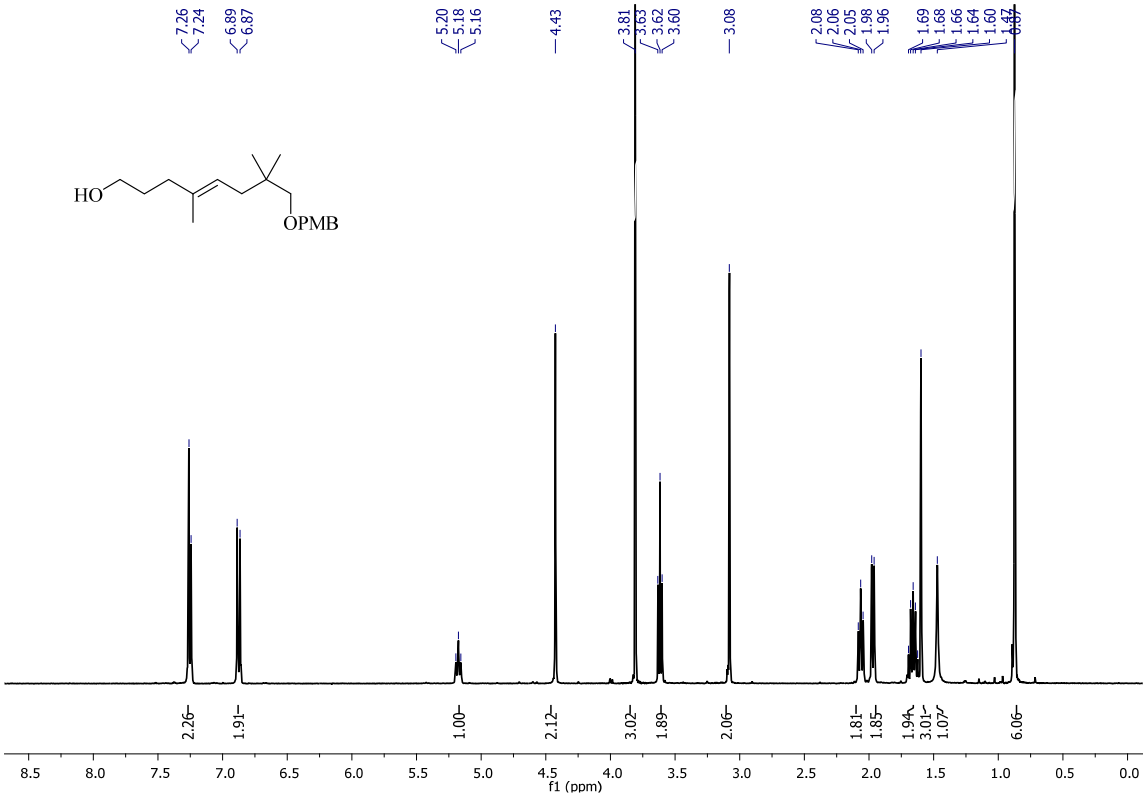
^{13}C NMR of compound 17 (125 MHz, $CDCl_3$)



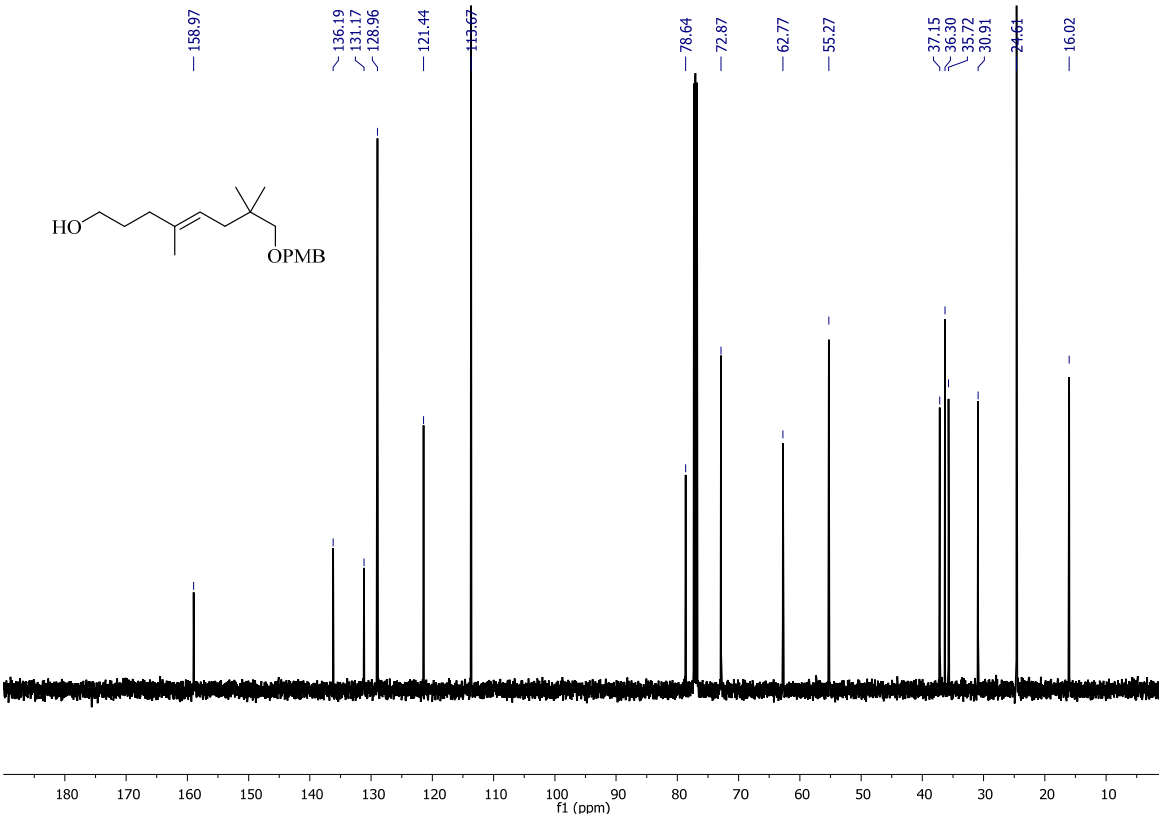
DEPT-135 of compound 17 (125 MHz, $CDCl_3$)



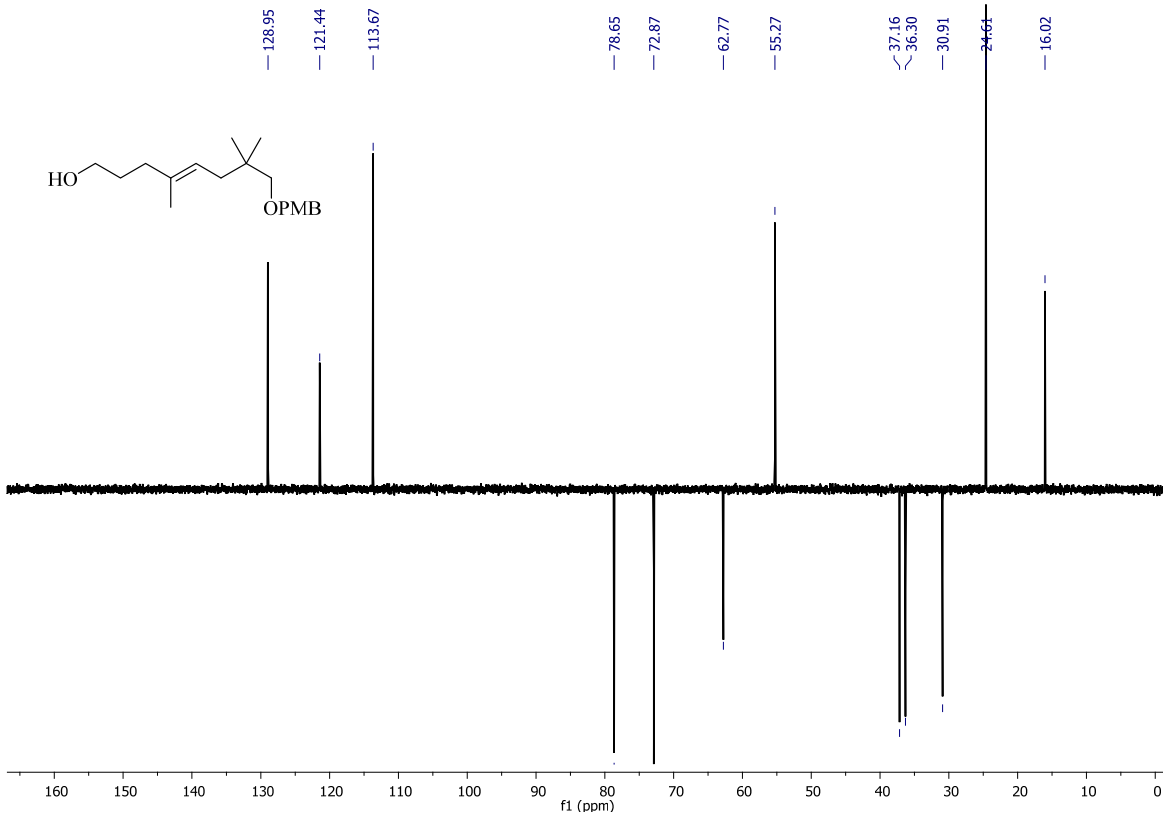
^{1}H NMR of compound 18 (400 MHz, $CDCl_3$)



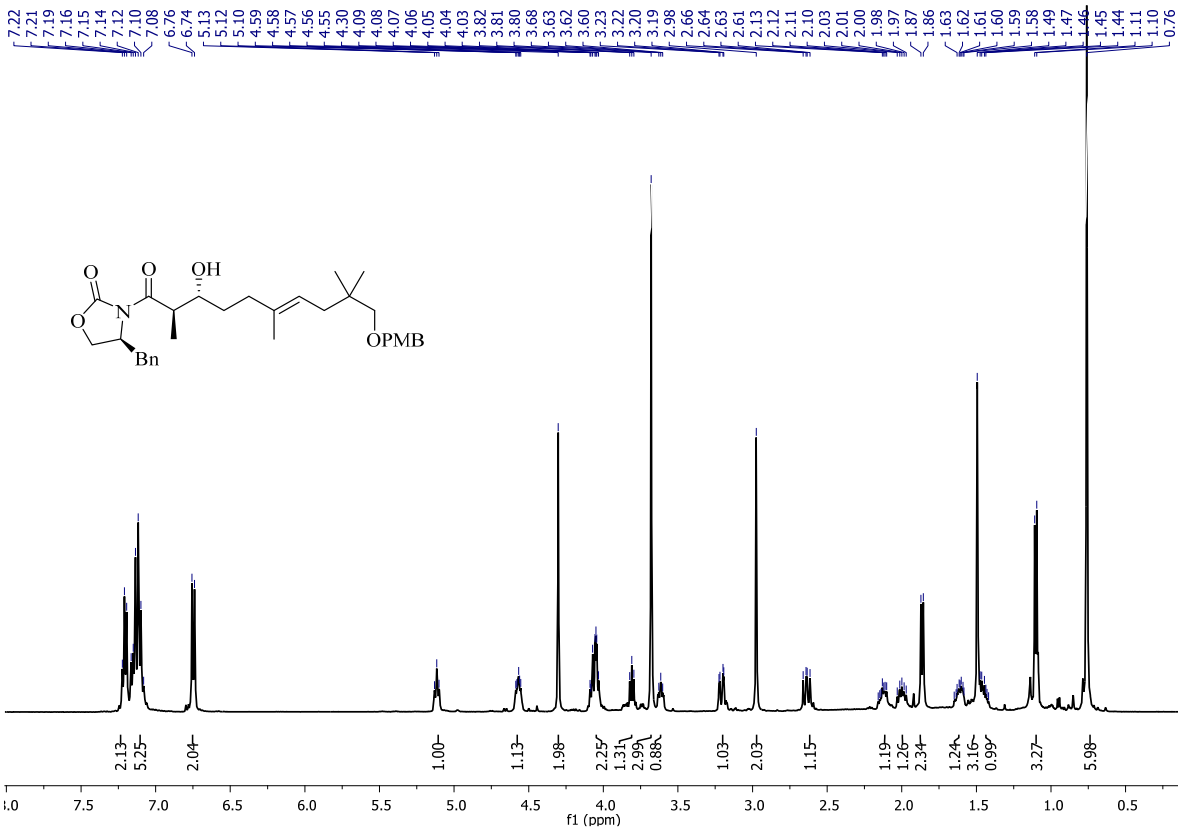
^{13}C NMR of compound 18 (125 MHz, $CDCl_3$)



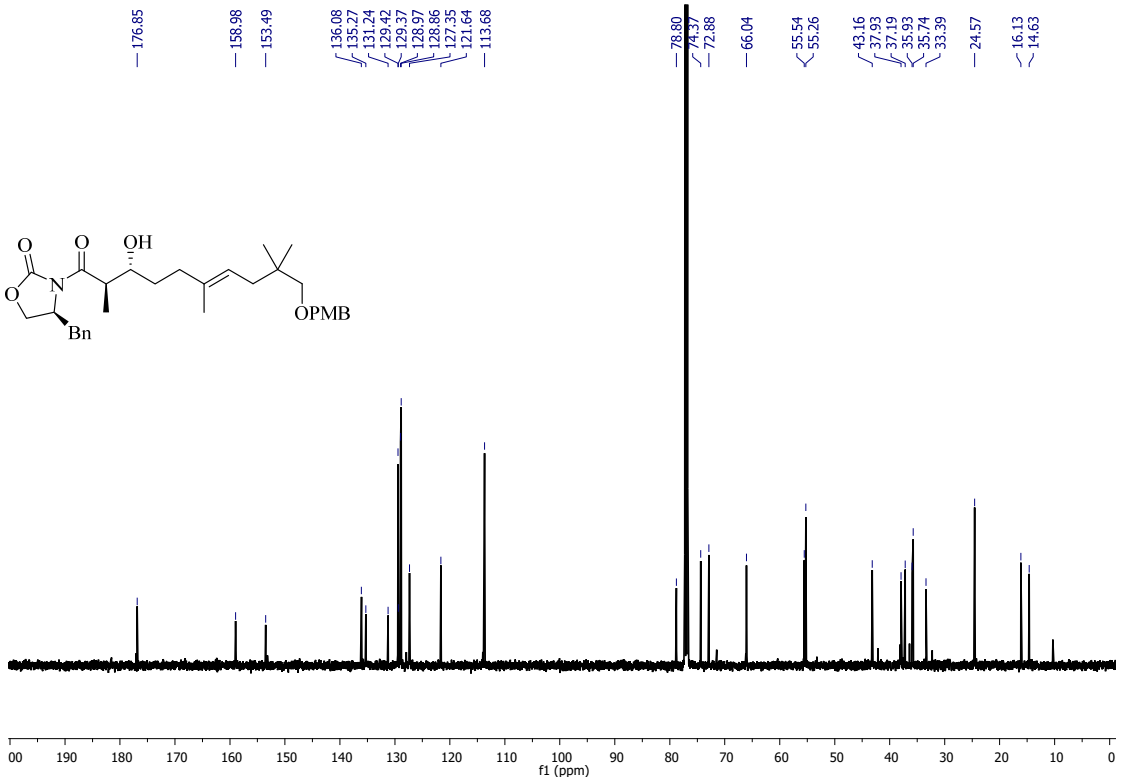
DEPT-135 of compound 18 (125 MHz, $CDCl_3$)



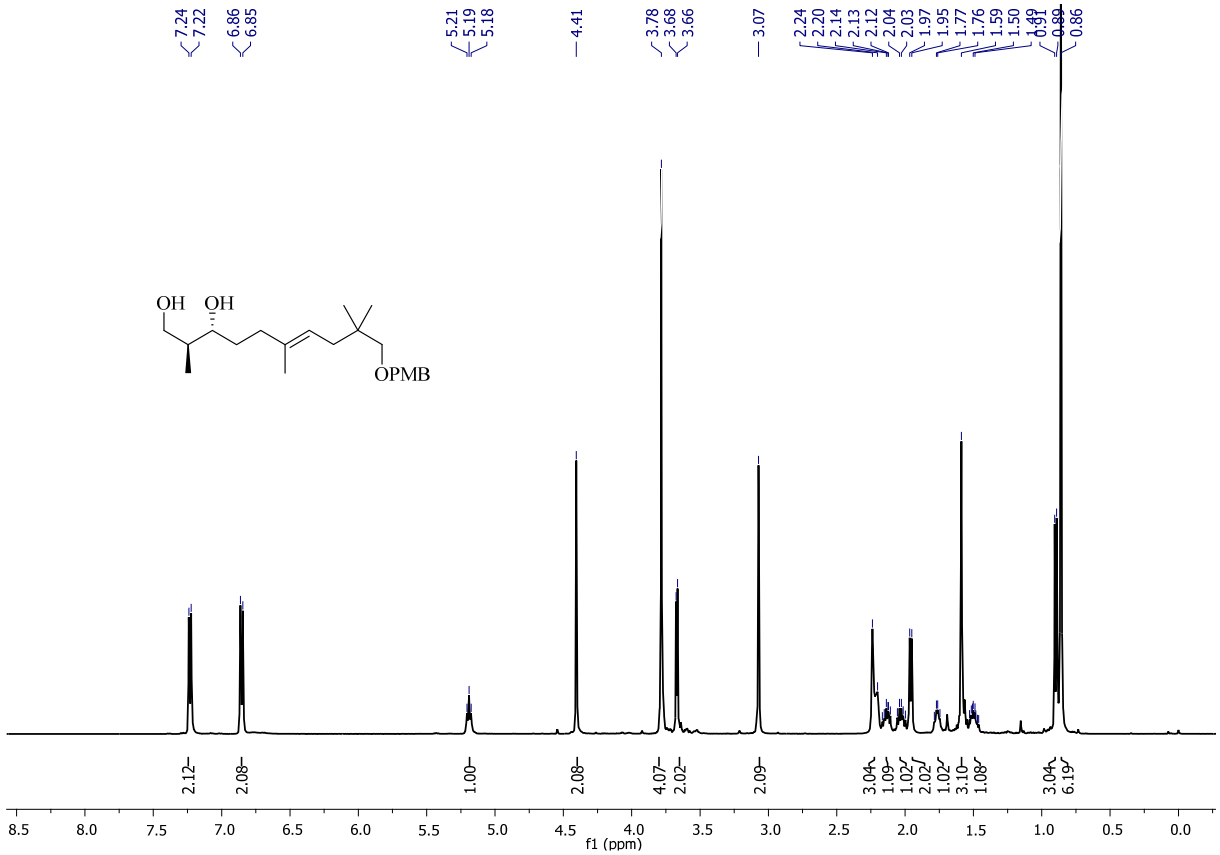
^{1}H NMR of compound 21 (500 MHz, $CDCl_3$)



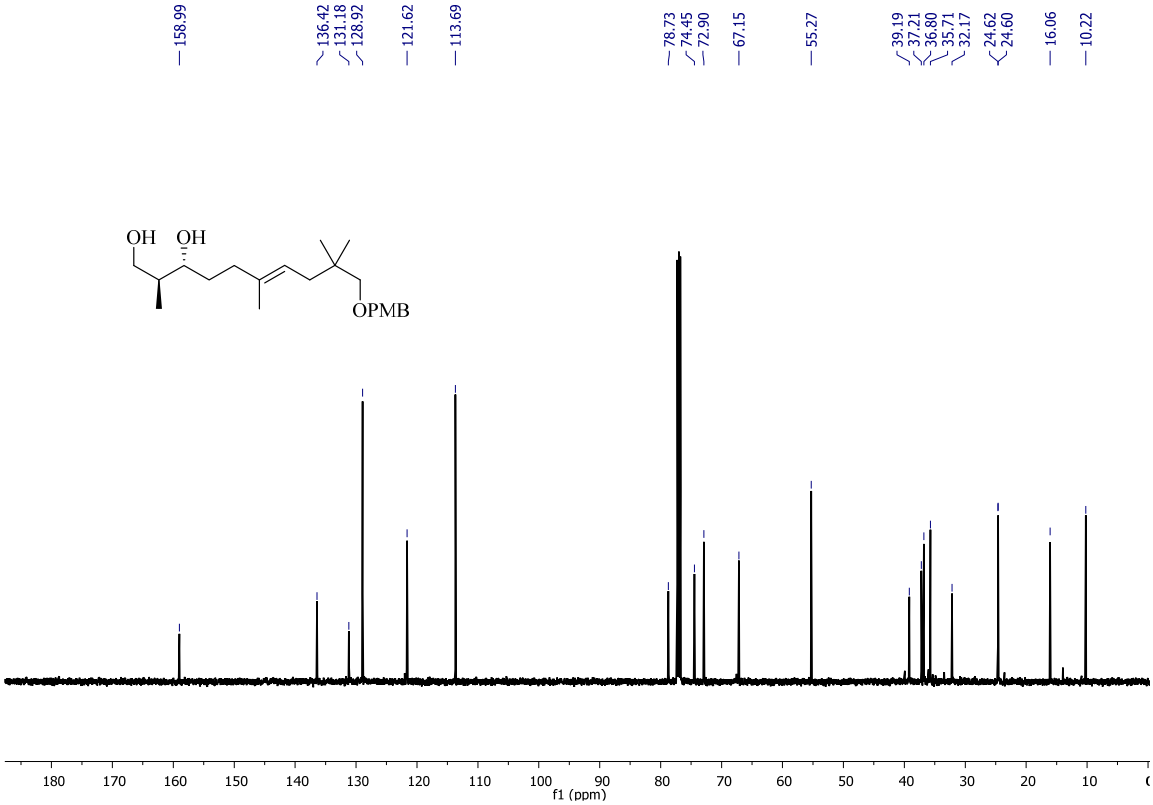
^{13}C NMR of compound 21 (125 MHz, $CDCl_3$)



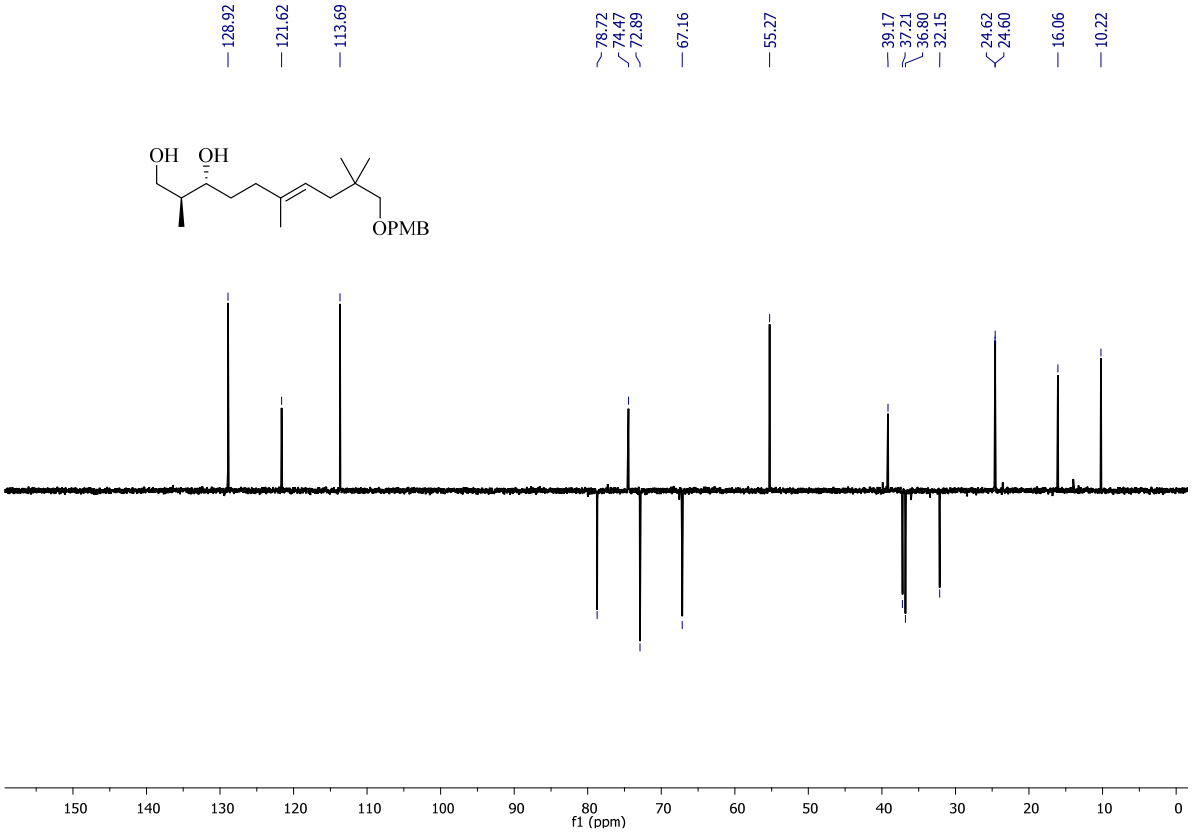
^{1}H NMR of compound 22 (500 MHz, $CDCl_3$)



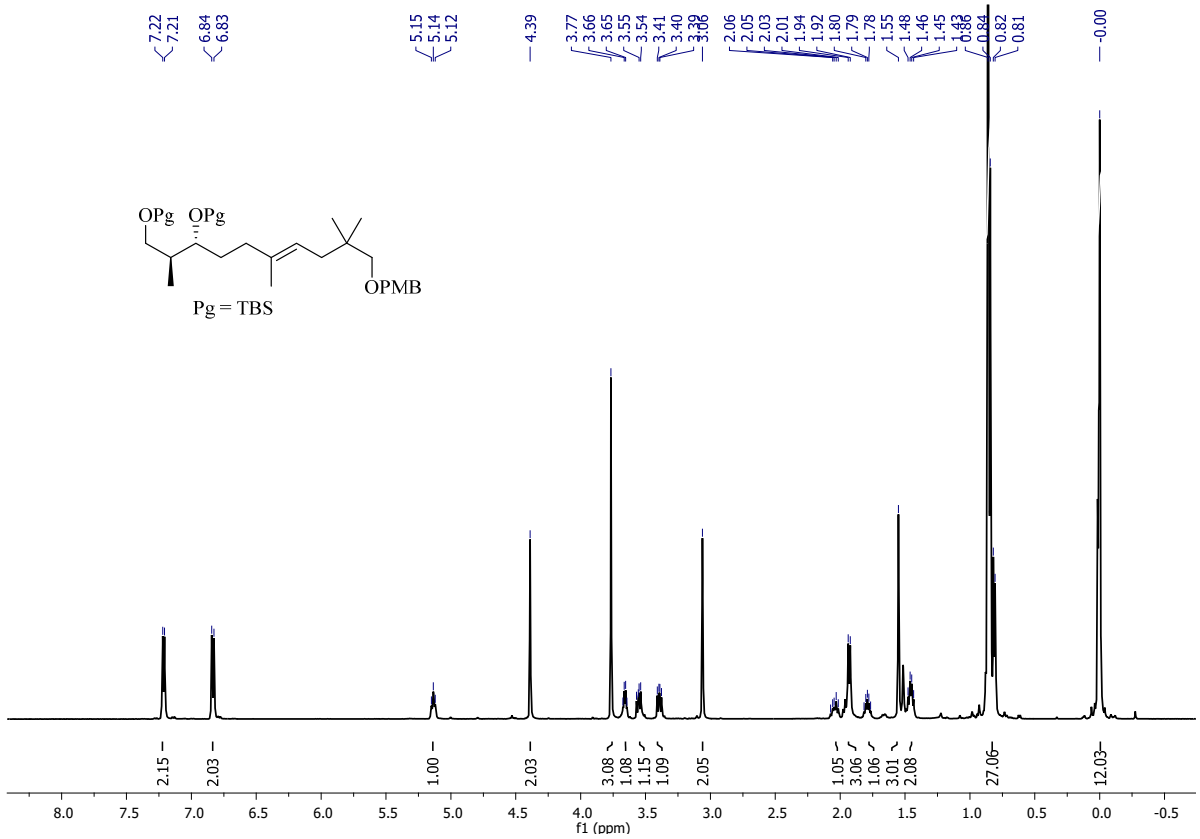
^{13}C NMR of compound 22 (125 MHz, $CDCl_3$)



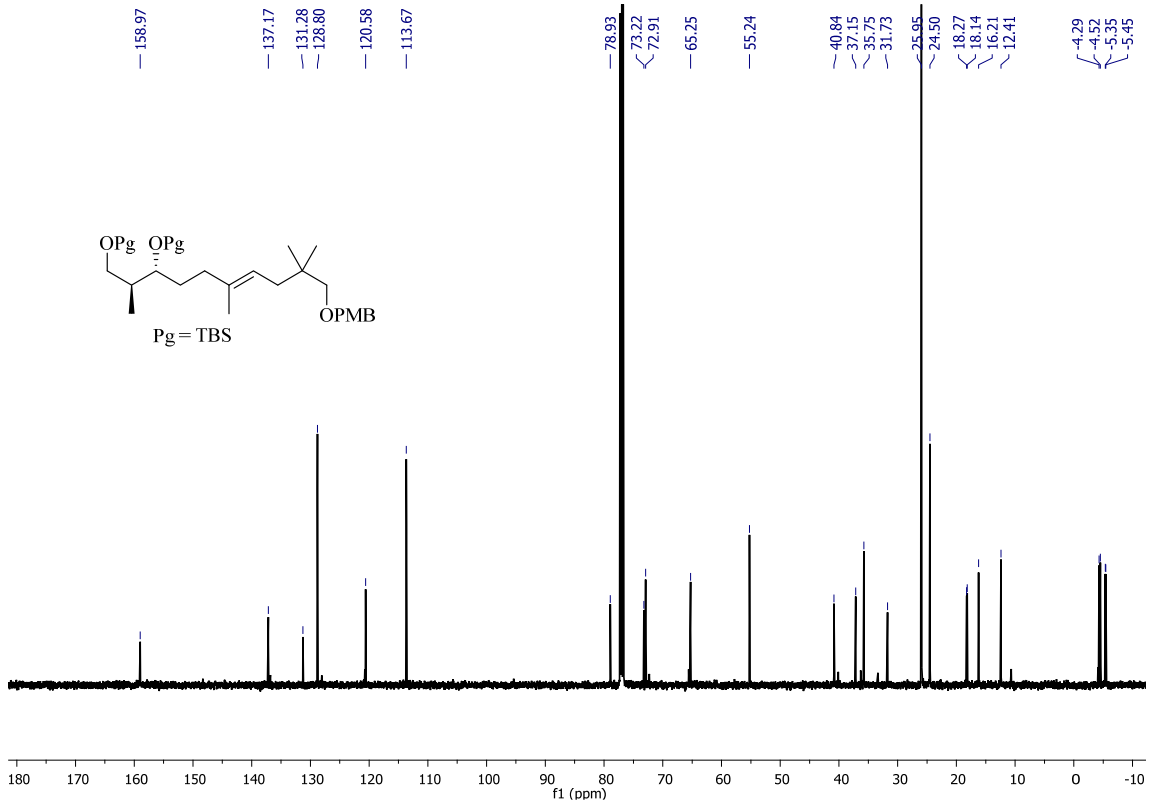
DEPT-135 of compound 22 (125 MHz, $CDCl_3$)



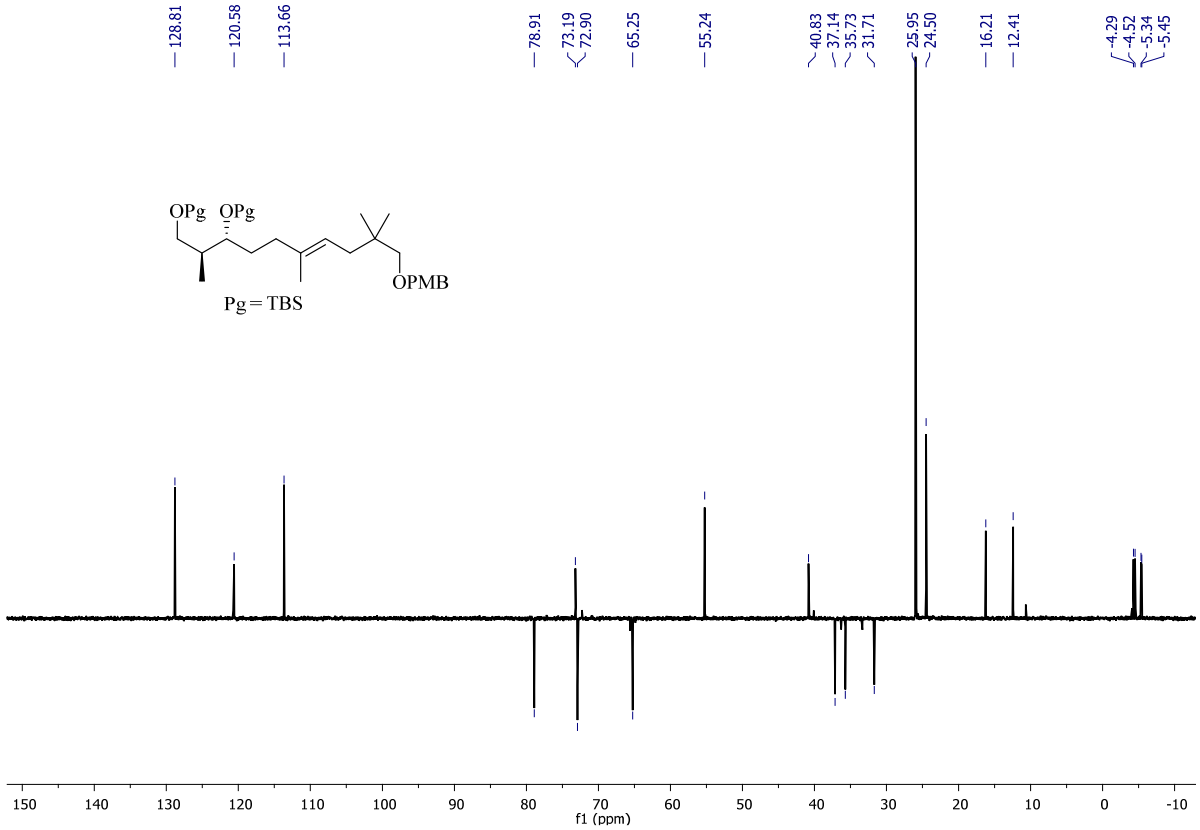
^{1}H NMR of compound 23 (500 MHz, $CDCl_3$)



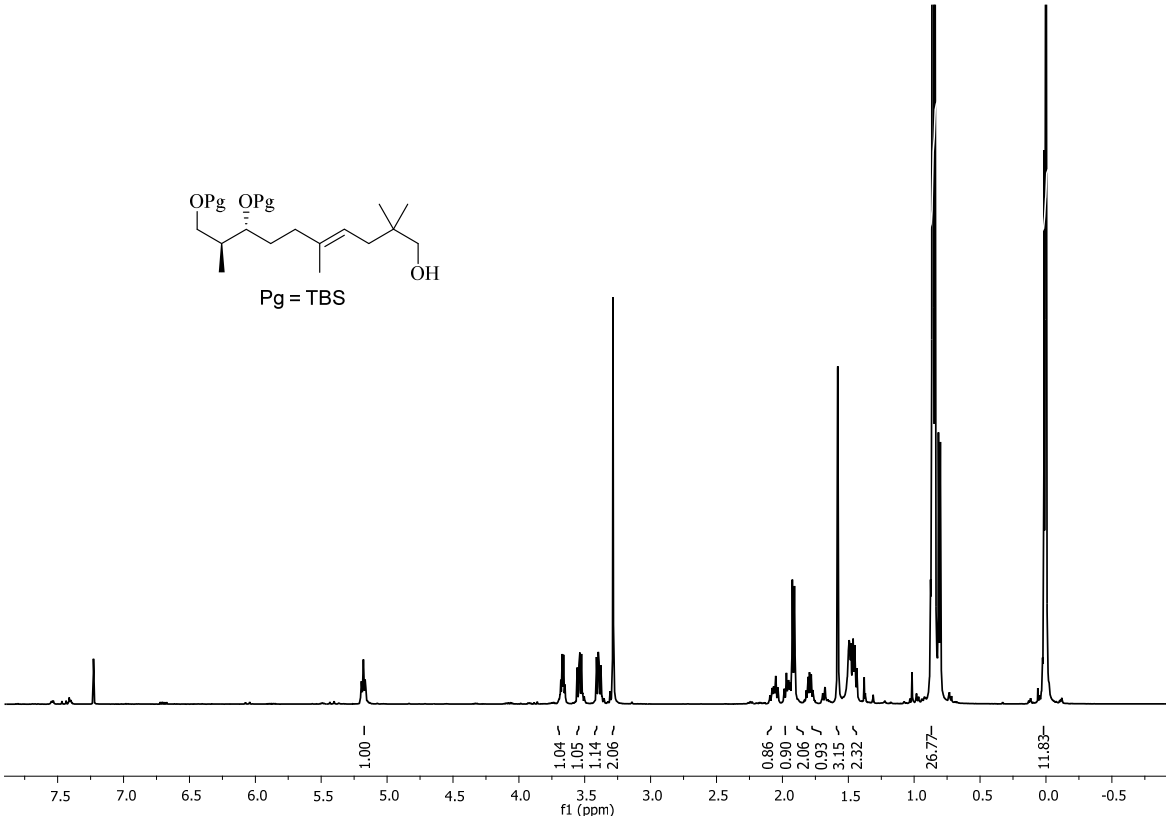
^{13}C NMR of compound 23 (125 MHz, $CDCl_3$)



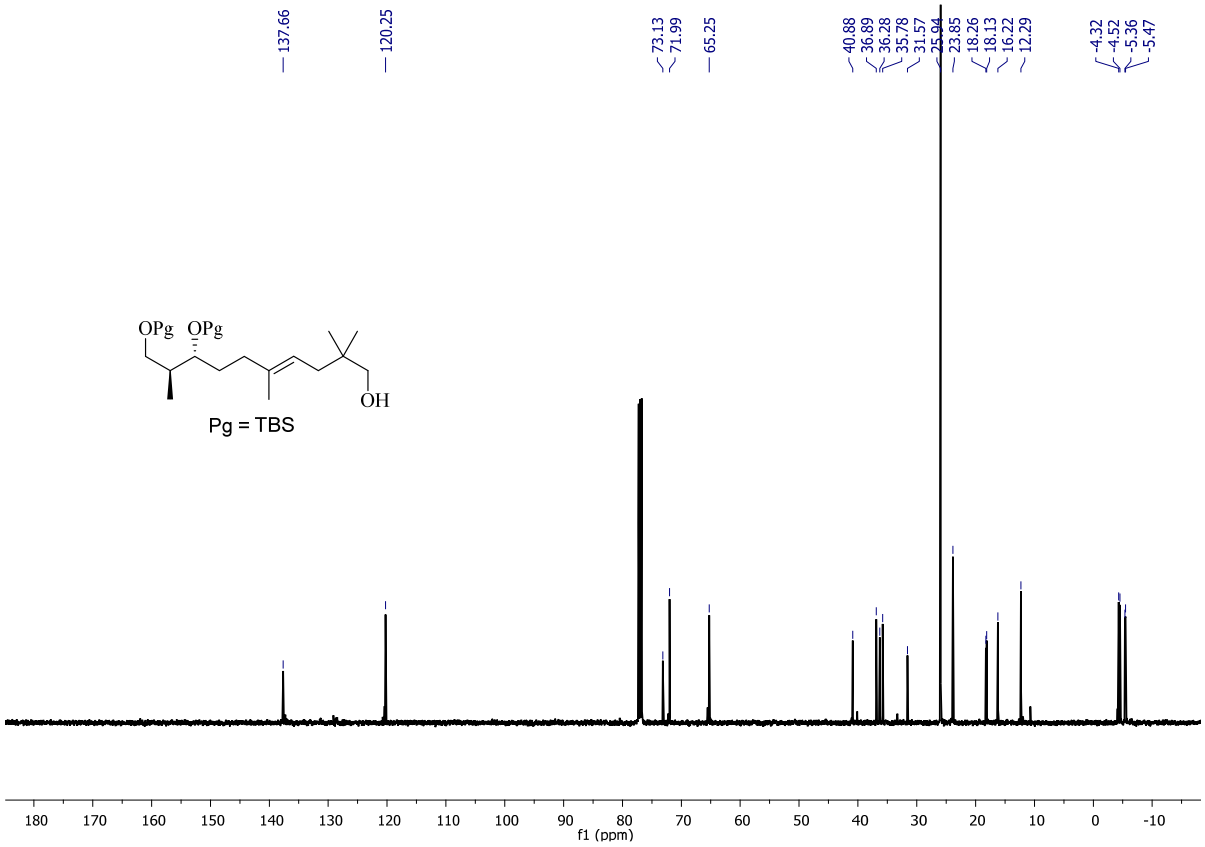
DEPT-135 of compound 23 (125 MHz, $CDCl_3$)



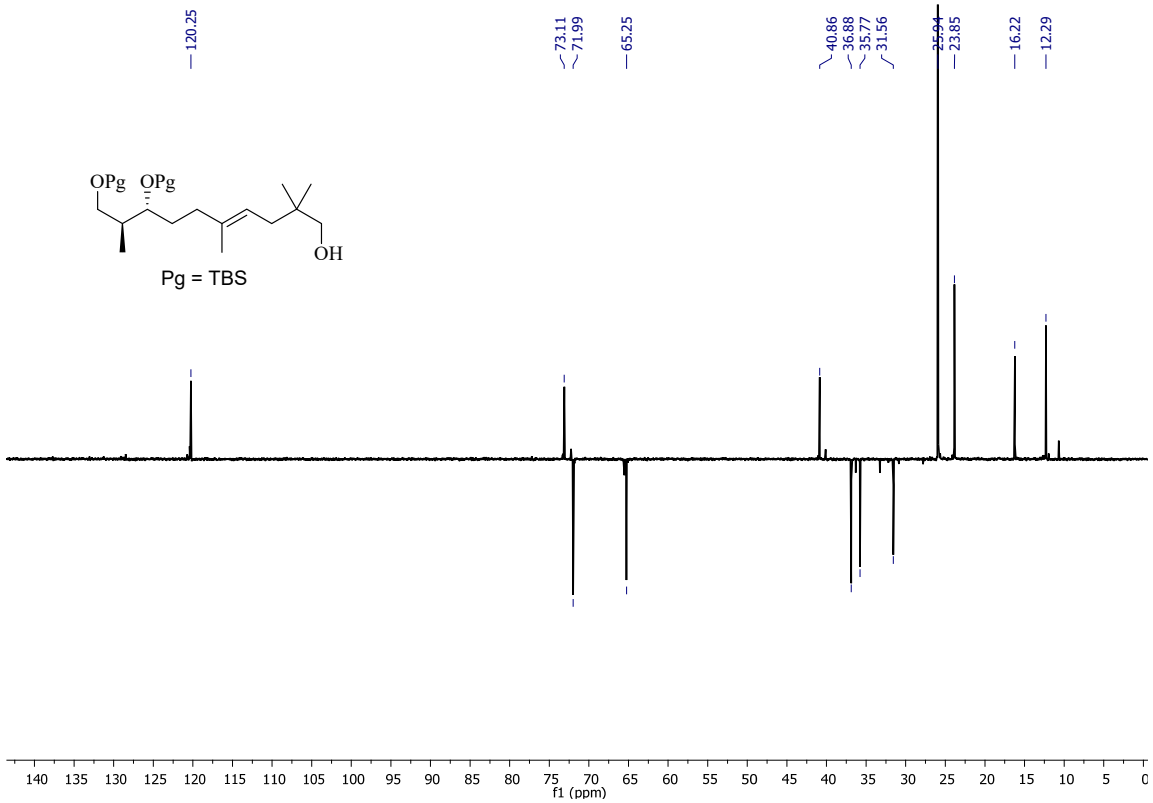
^{1}H NMR of compound 24 (500 MHz, $CDCl_3$)



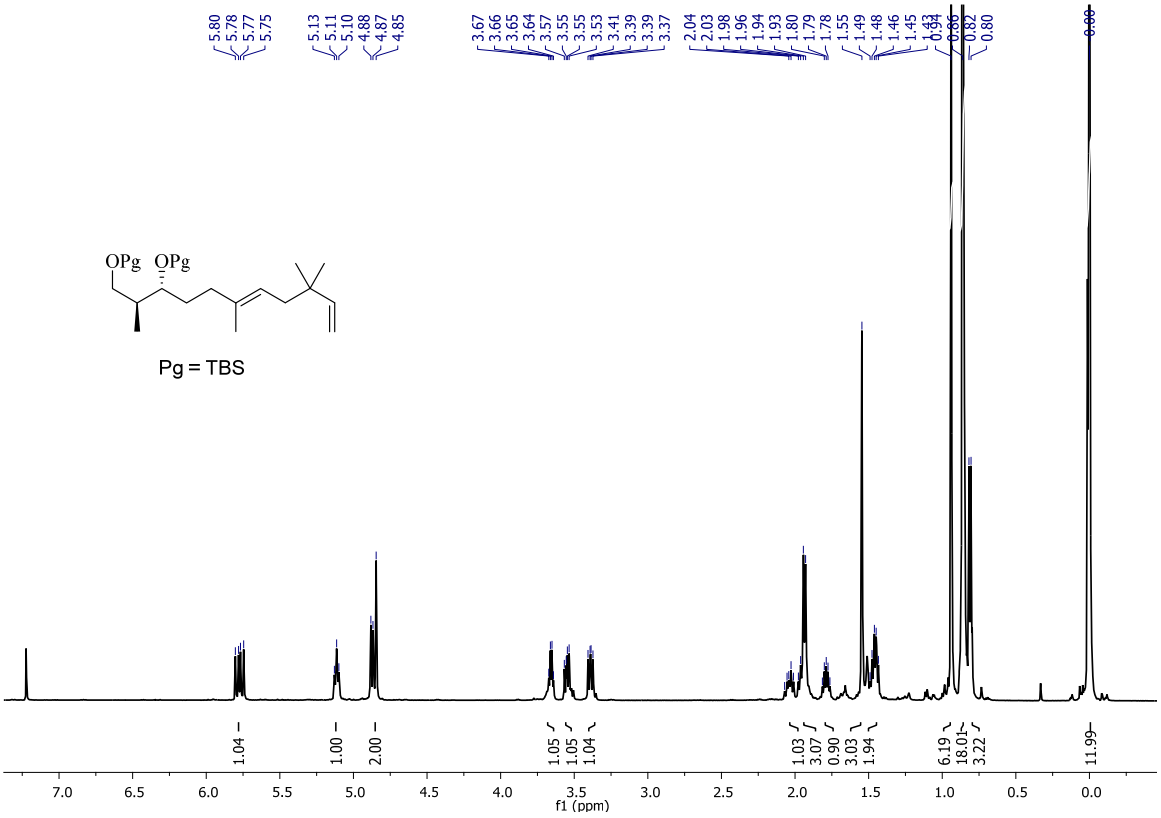
^{13}C NMR of compound 24 (125 MHz, $CDCl_3$)



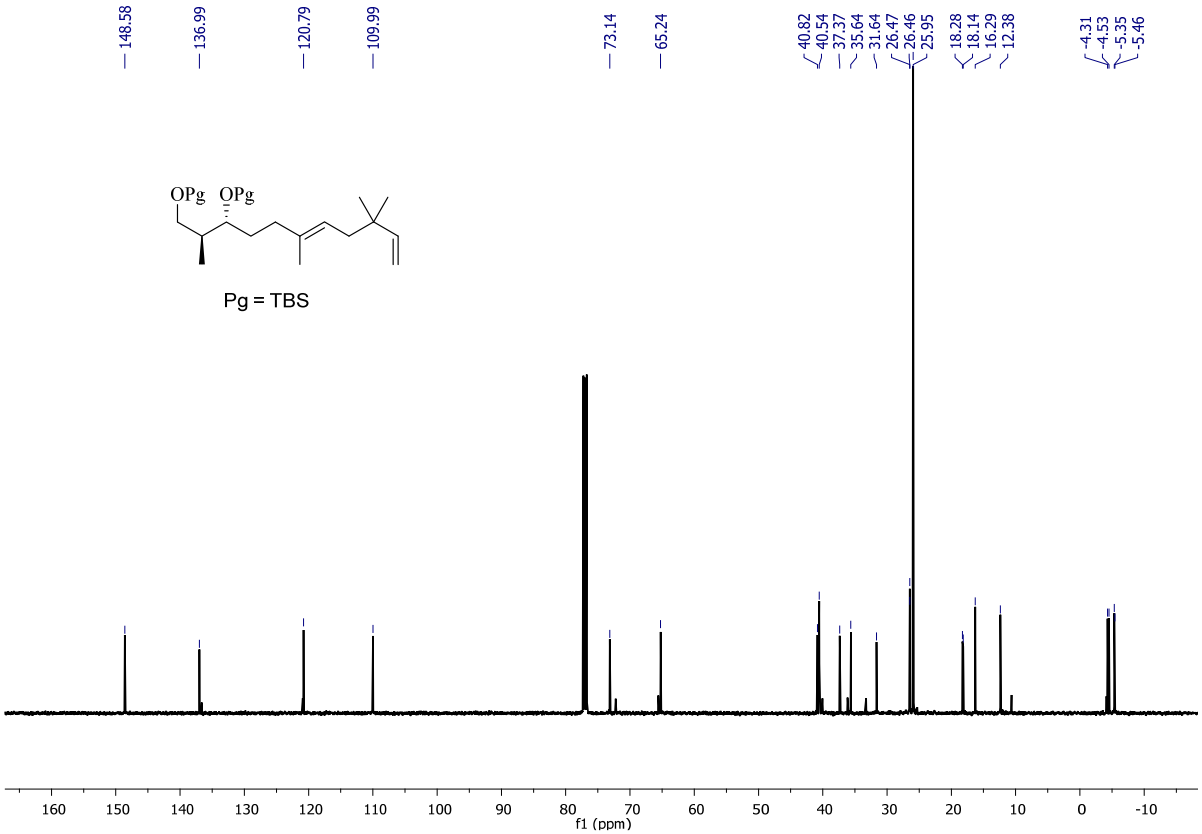
DEPT-135 of compound 24 (125 MHz, $CDCl_3$)



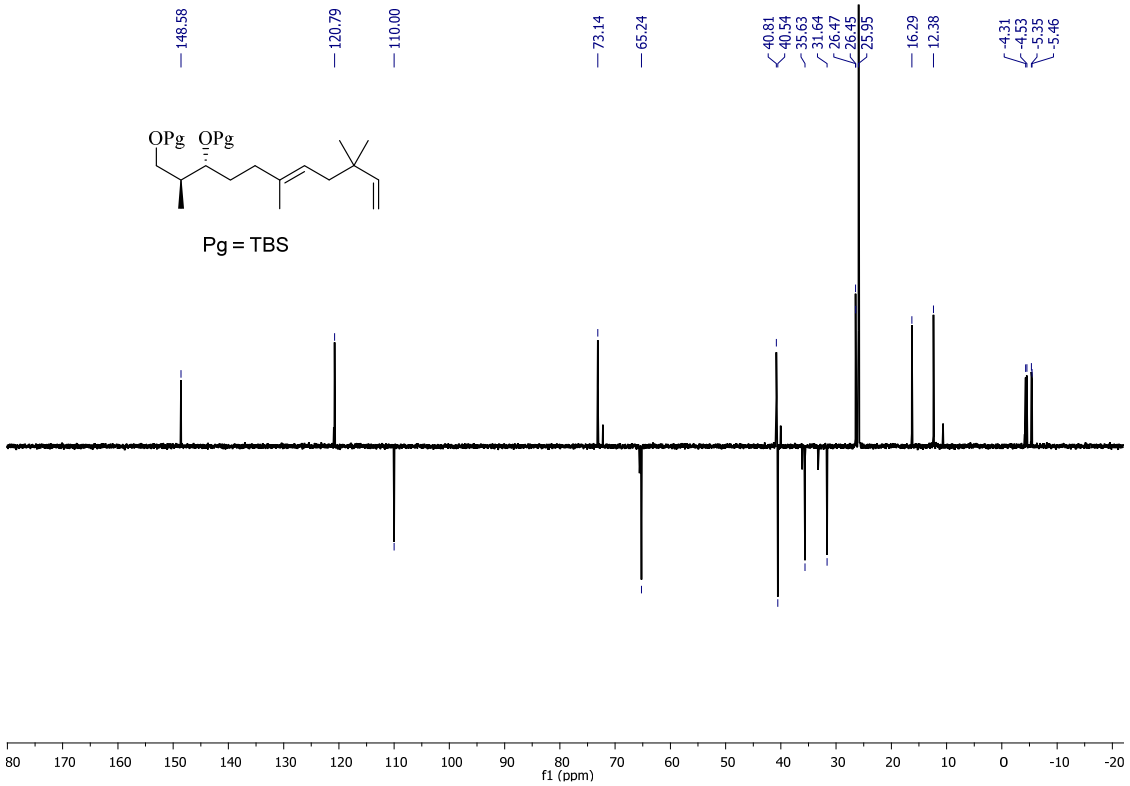
^{1}H NMR of compound 26 (500 MHz, $CDCl_3$)



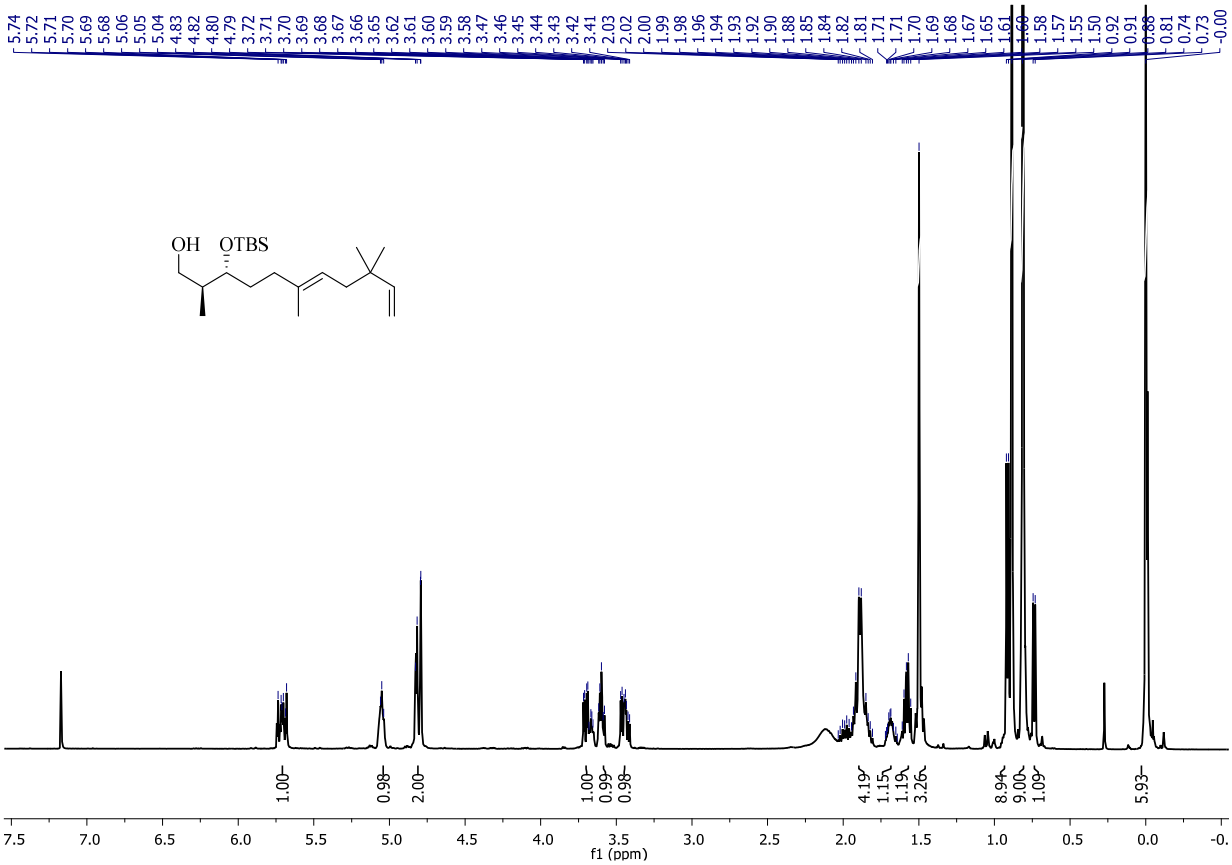
^{13}C NMR of compound 26 (125 MHz, $CDCl_3$)



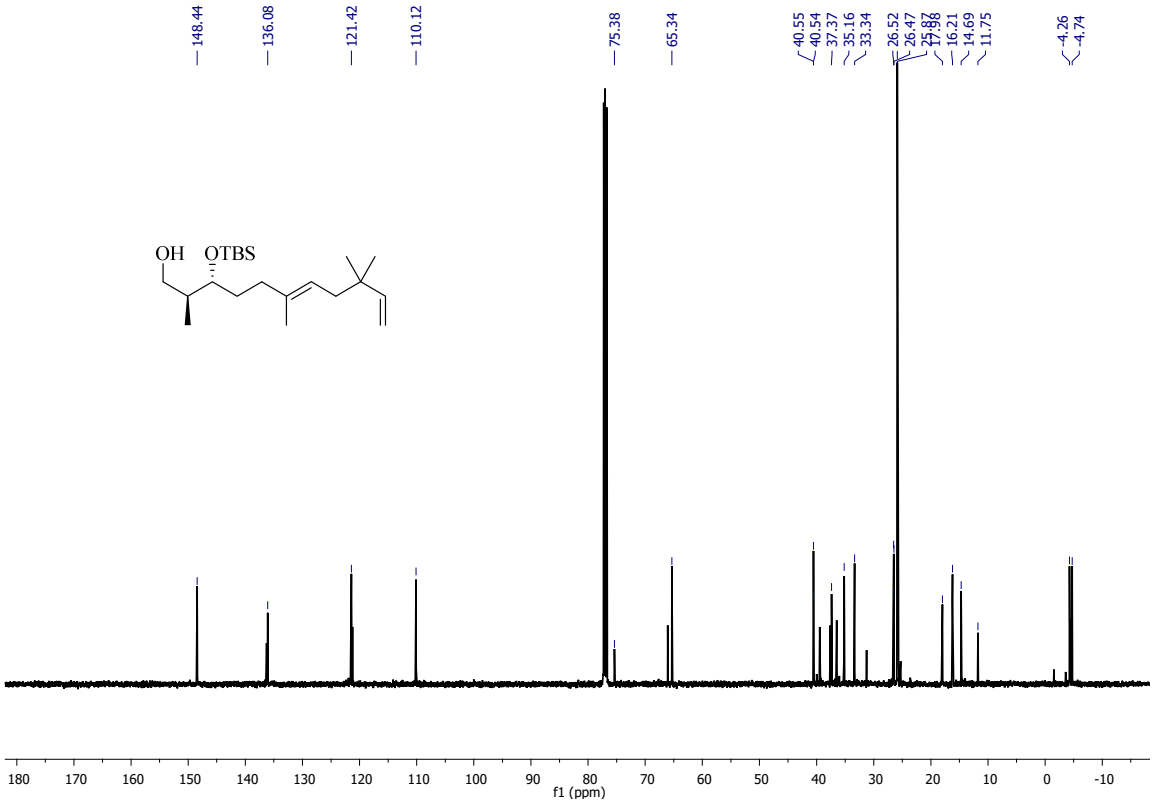
DEPT-135 of compound 26 (125 MHz, $CDCl_3$)



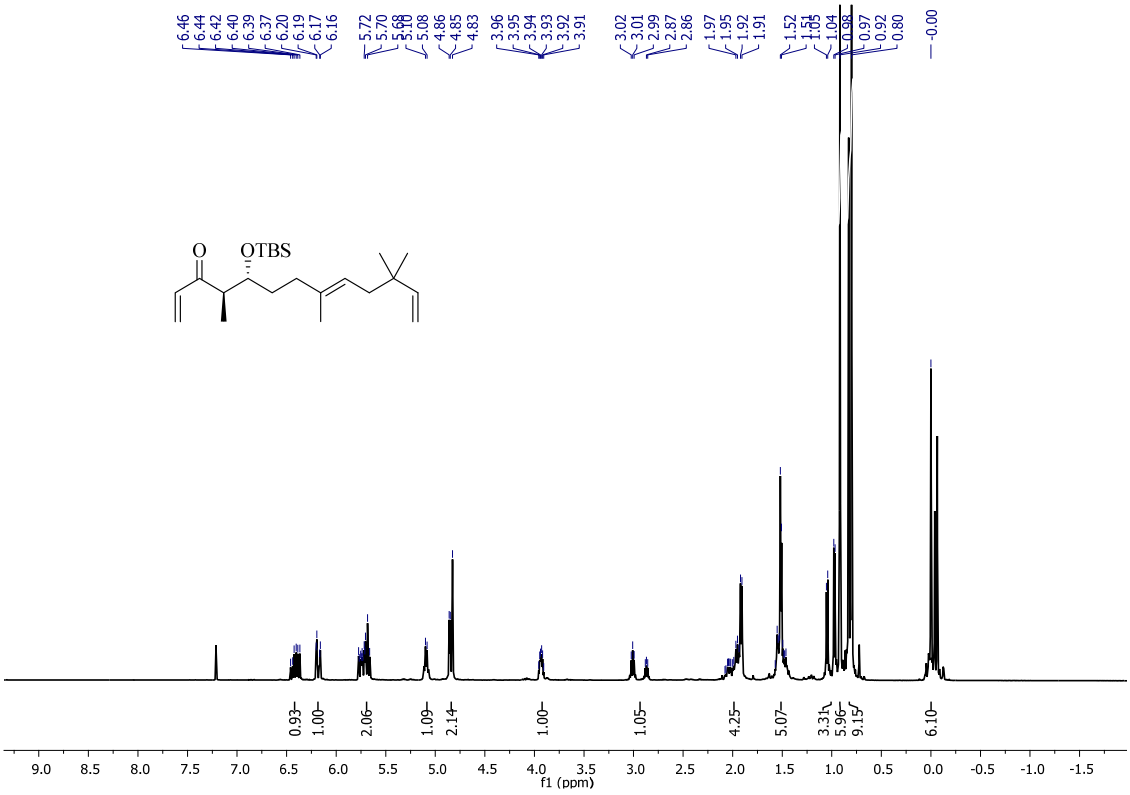
^{1}H NMR of compound 27 (500 MHz, $CDCl_3$)



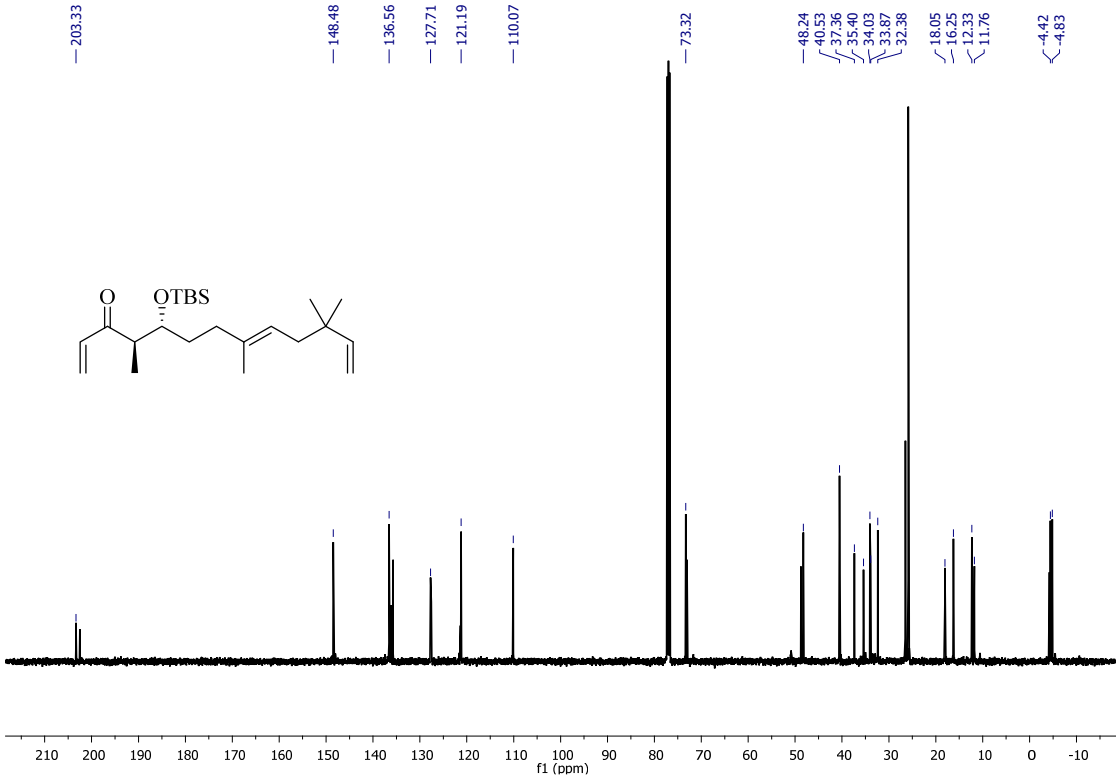
^{13}C NMR of compound 27 (125 MHz, $CDCl_3$)



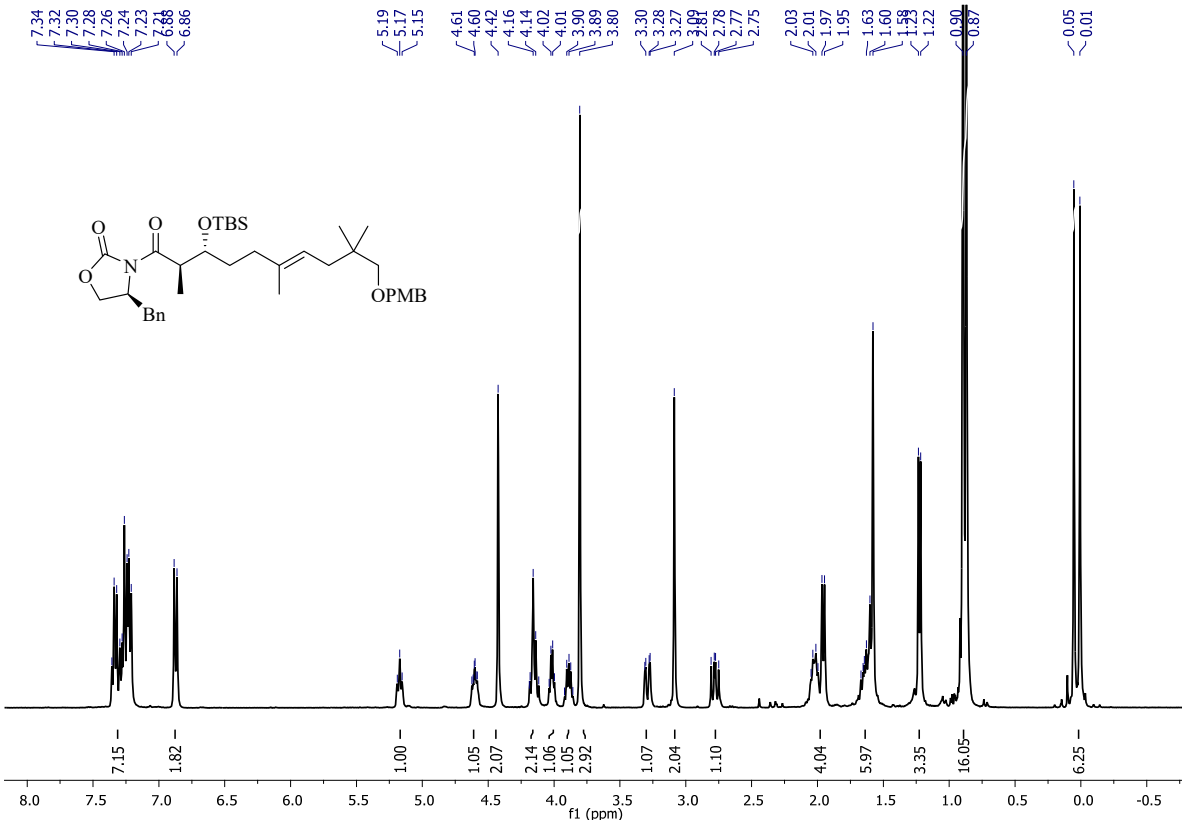
^{1}H NMR of compound 28 (500 MHz, $CDCl_3$)



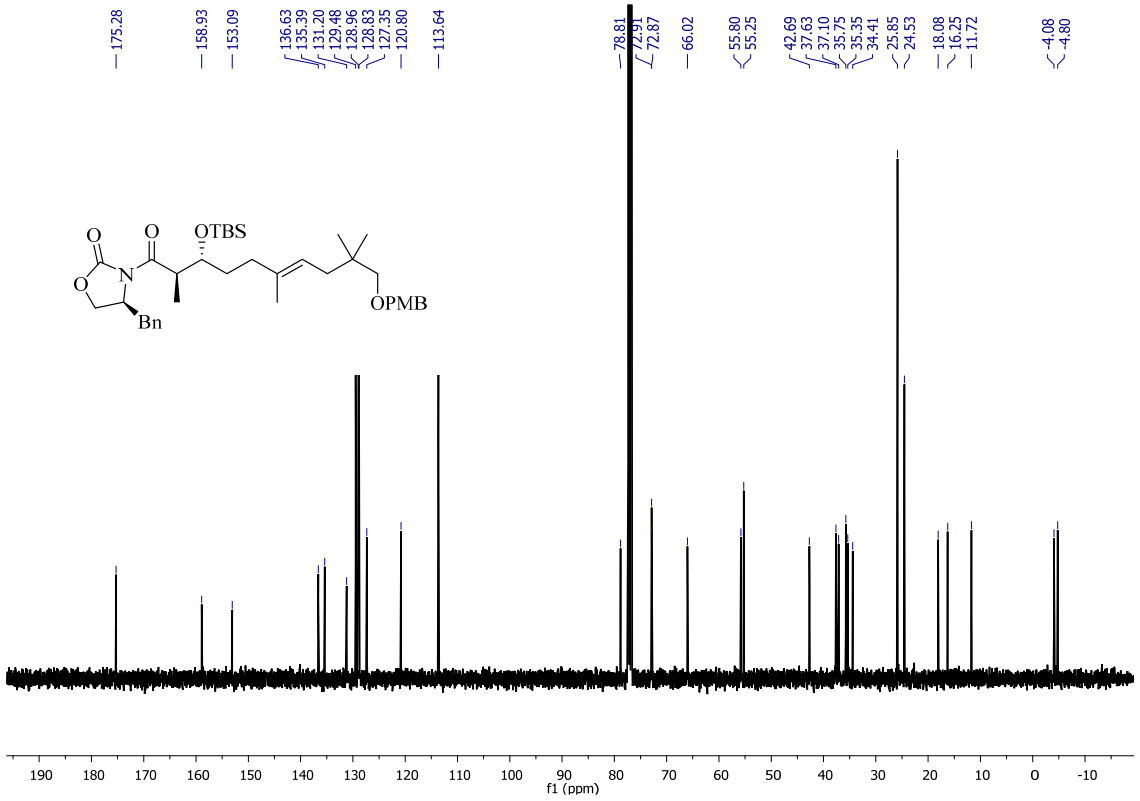
^{13}C NMR of compound 28 (125 MHz, $CDCl_3$)



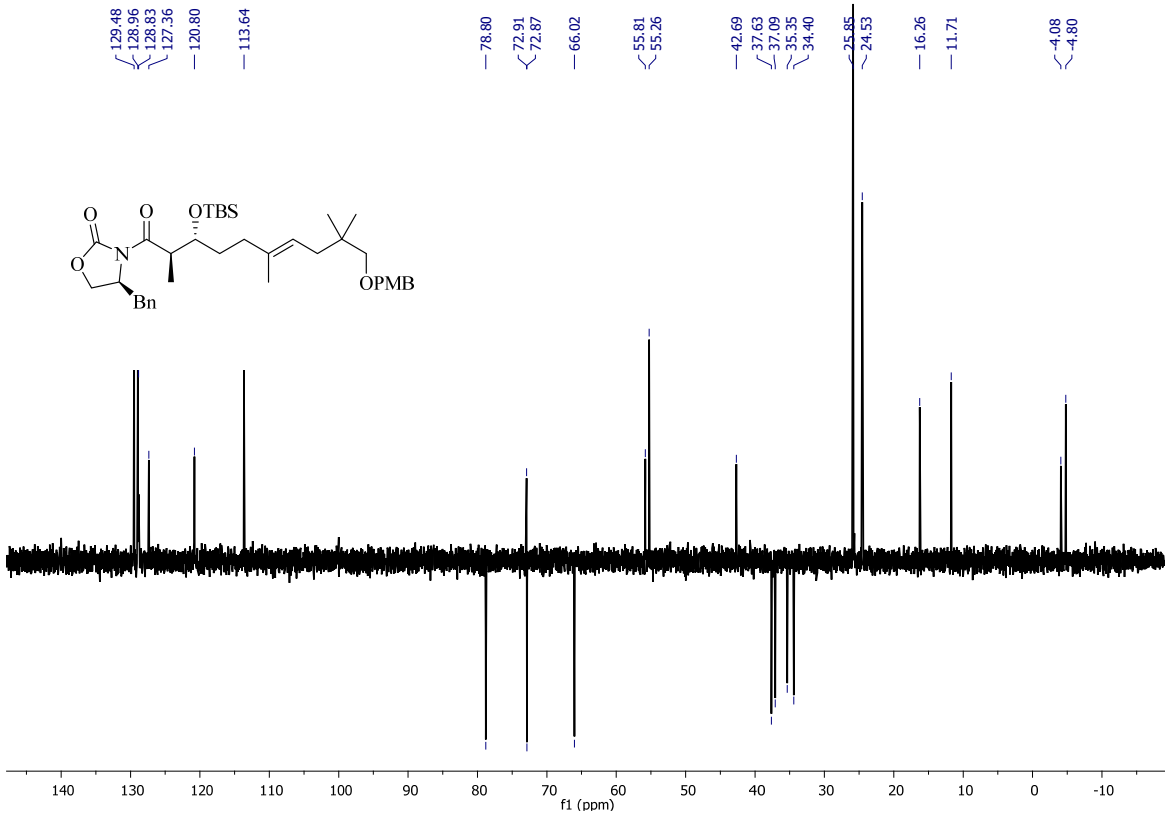
^{1}H NMR of compound 29 (500 MHz, $CDCl_3$)



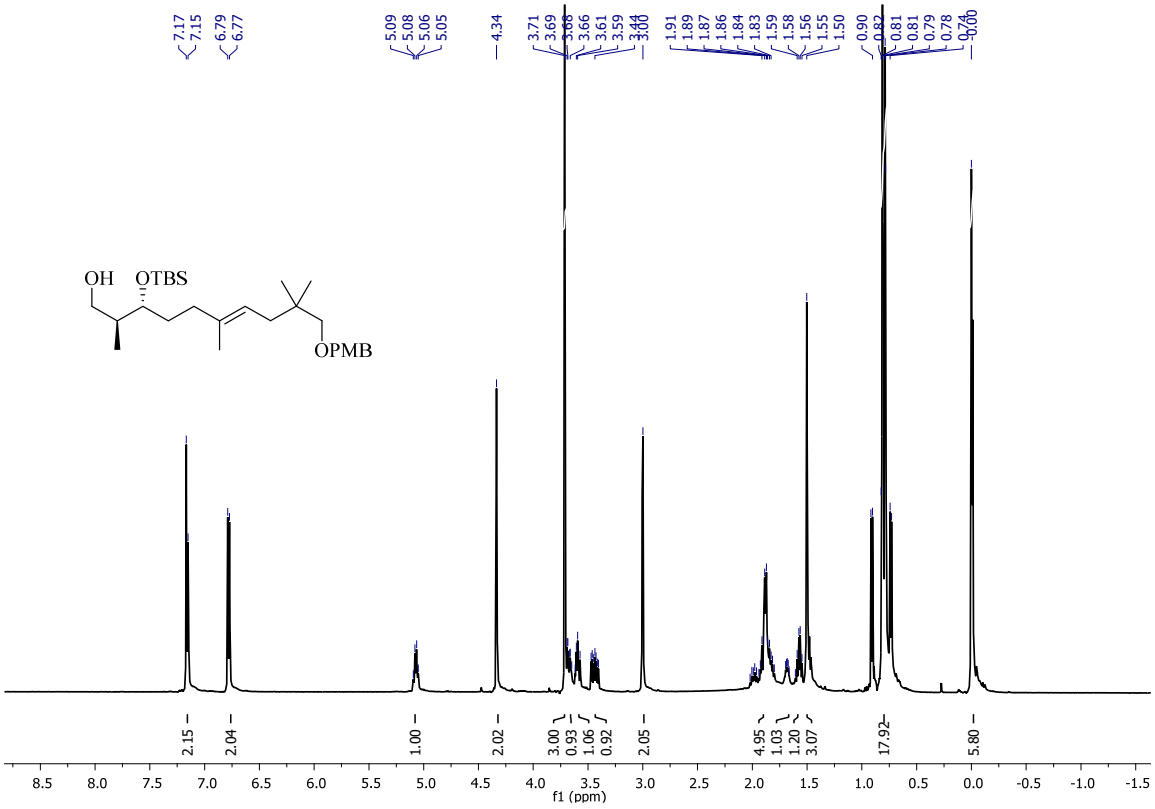
^{13}C NMR of compound 29 (125 MHz, $CDCl_3$)



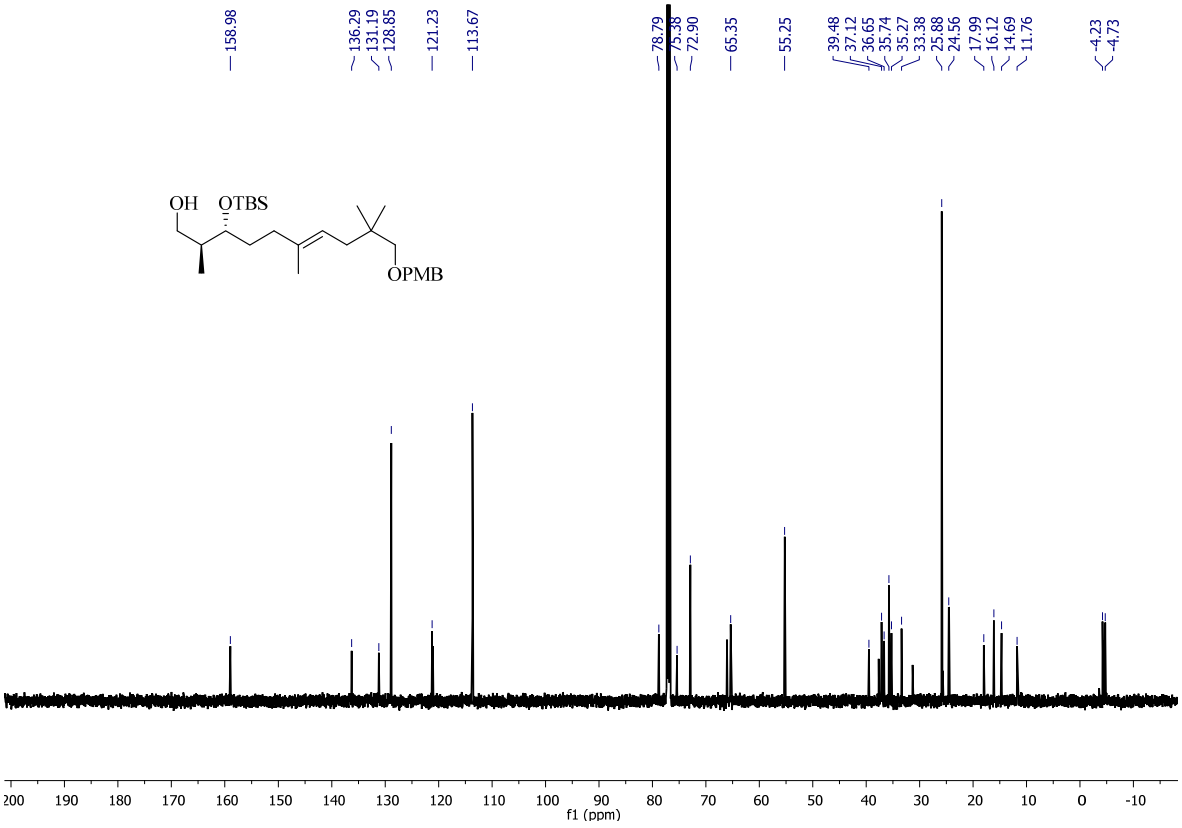
DEPT-135 of compound 29 (125 MHz, $CDCl_3$)



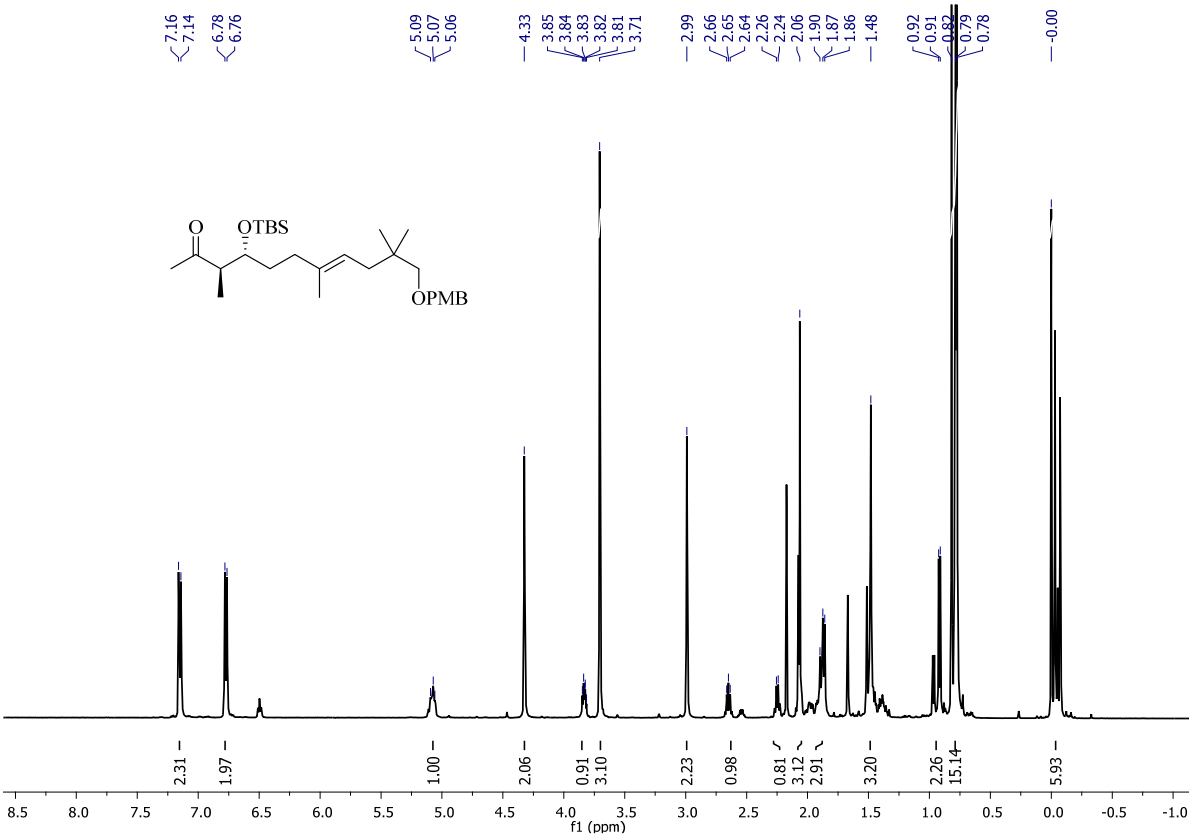
^{1}H NMR of compound 30 (500 MHz, $CDCl_3$)



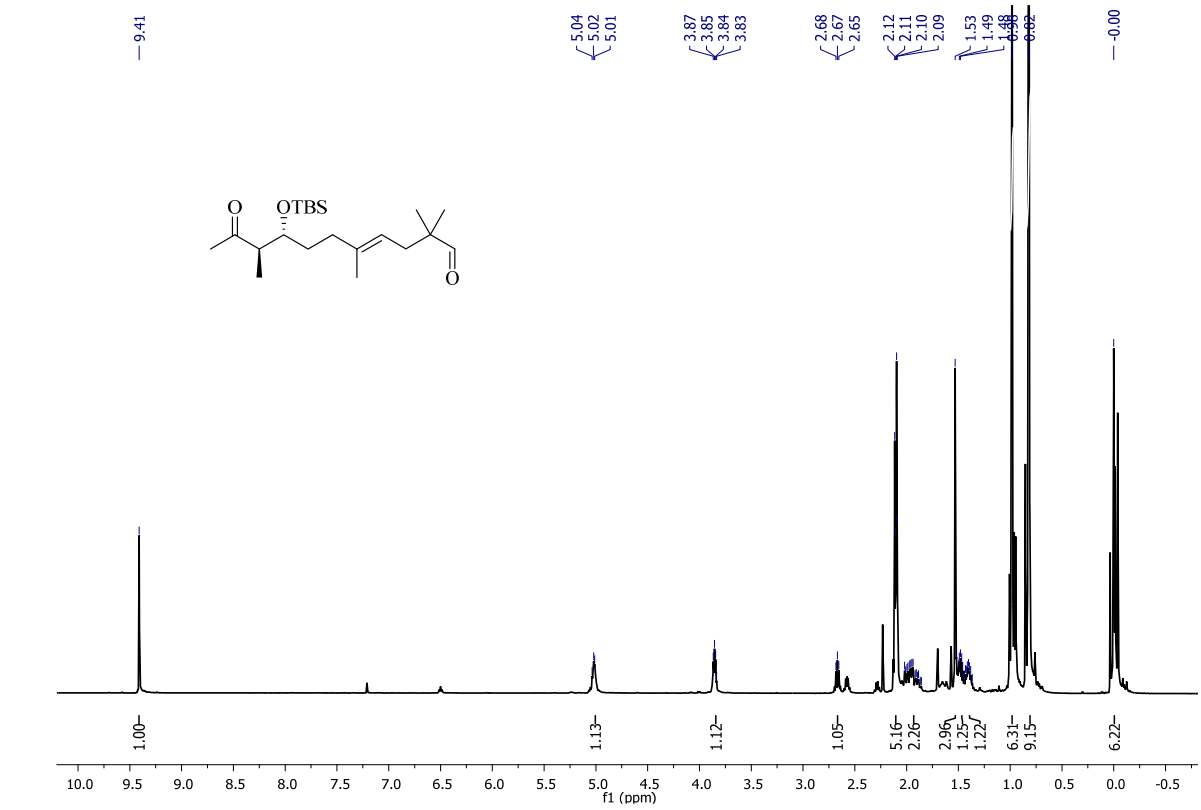
^{13}C NMR of compound 30 (125 MHz, $CDCl_3$)



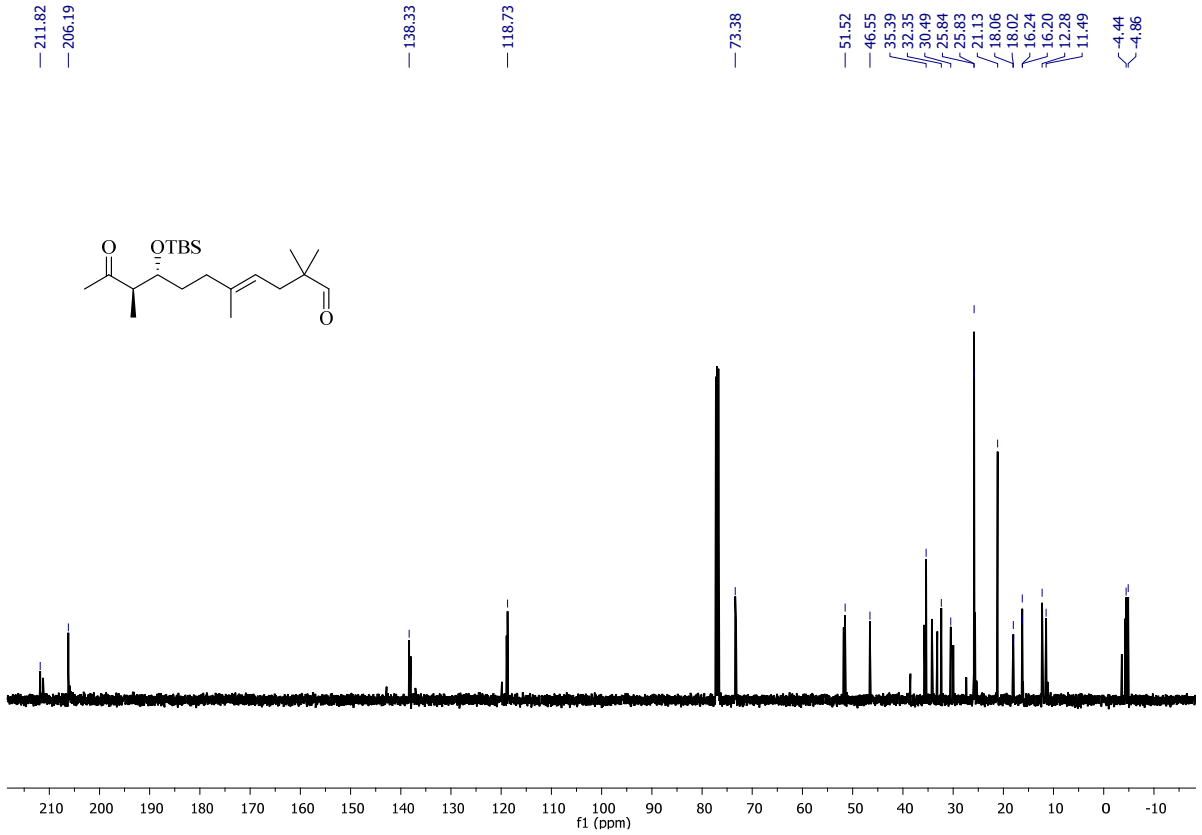
^{1}H NMR of compound 31 (500 MHz, $CDCl_3$)



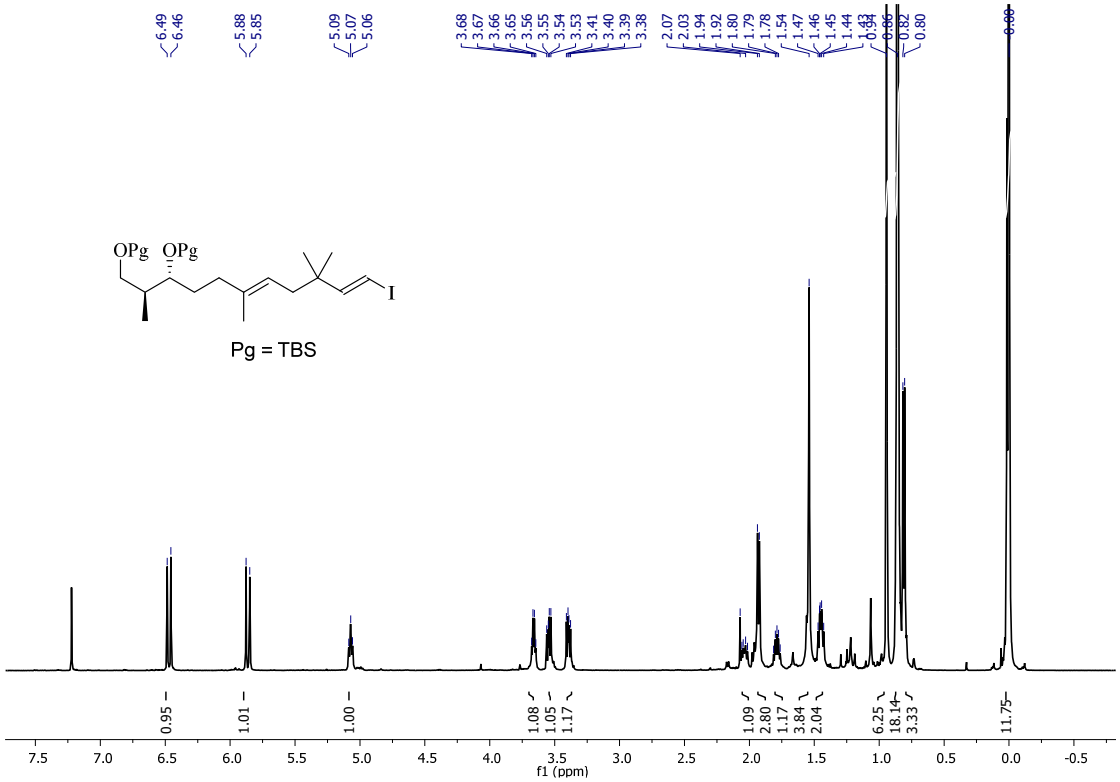
^{1}H NMR of compound 32 (500 MHz, $CDCl_3$)



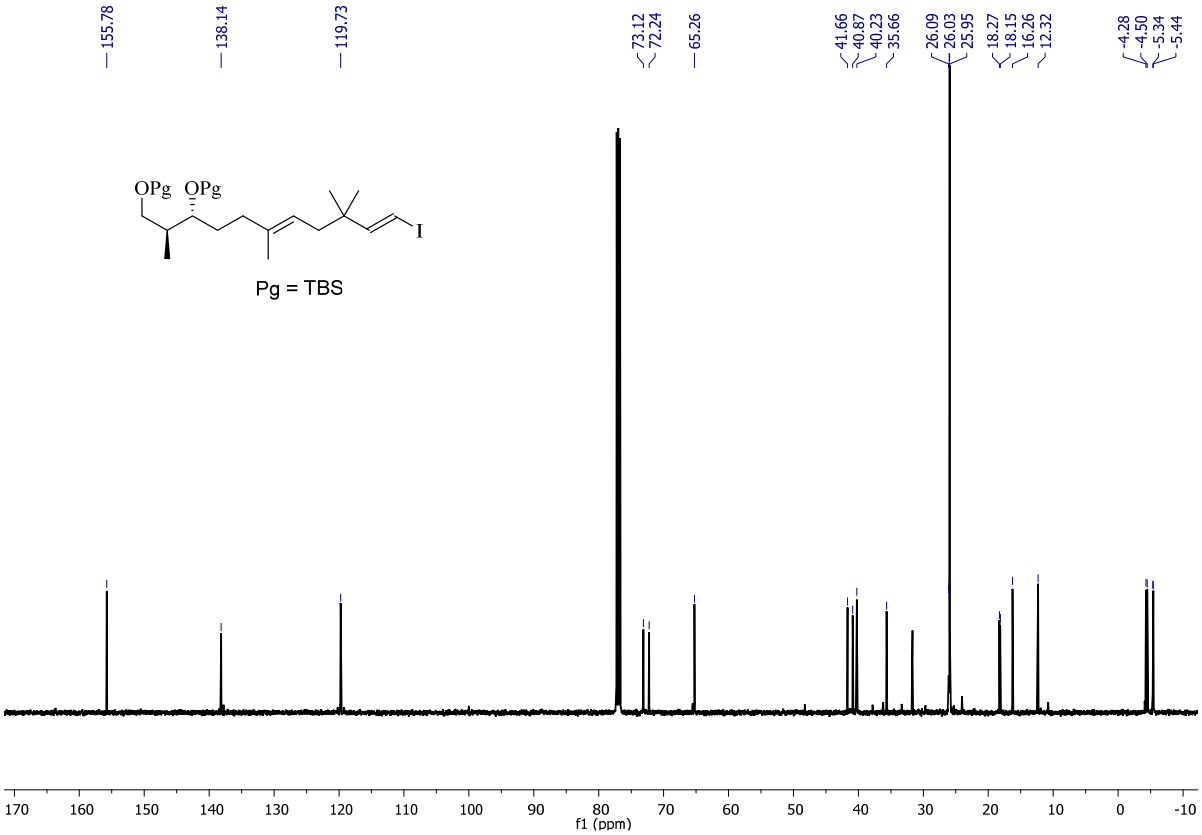
^{13}C NMR of compound 32 (125 MHz, $CDCl_3$)



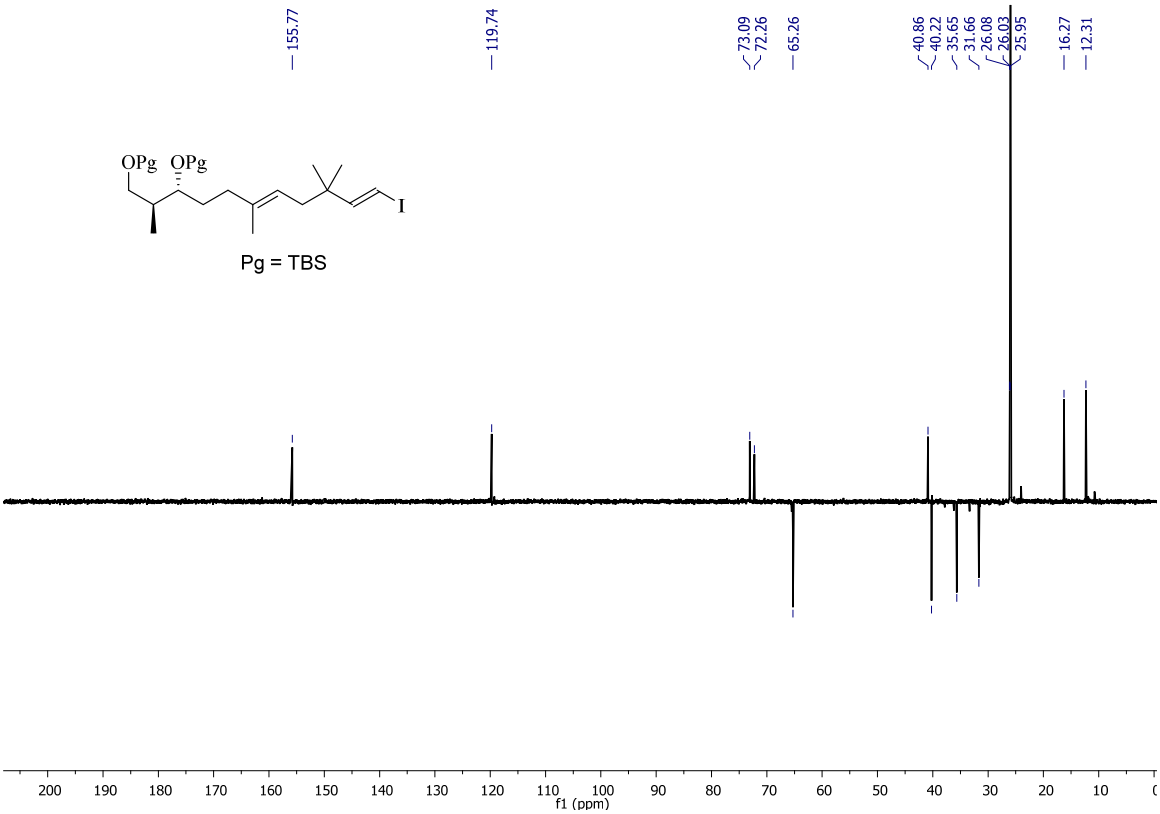
^{1}H NMR of compound 33 (500 MHz, $CDCl_3$)



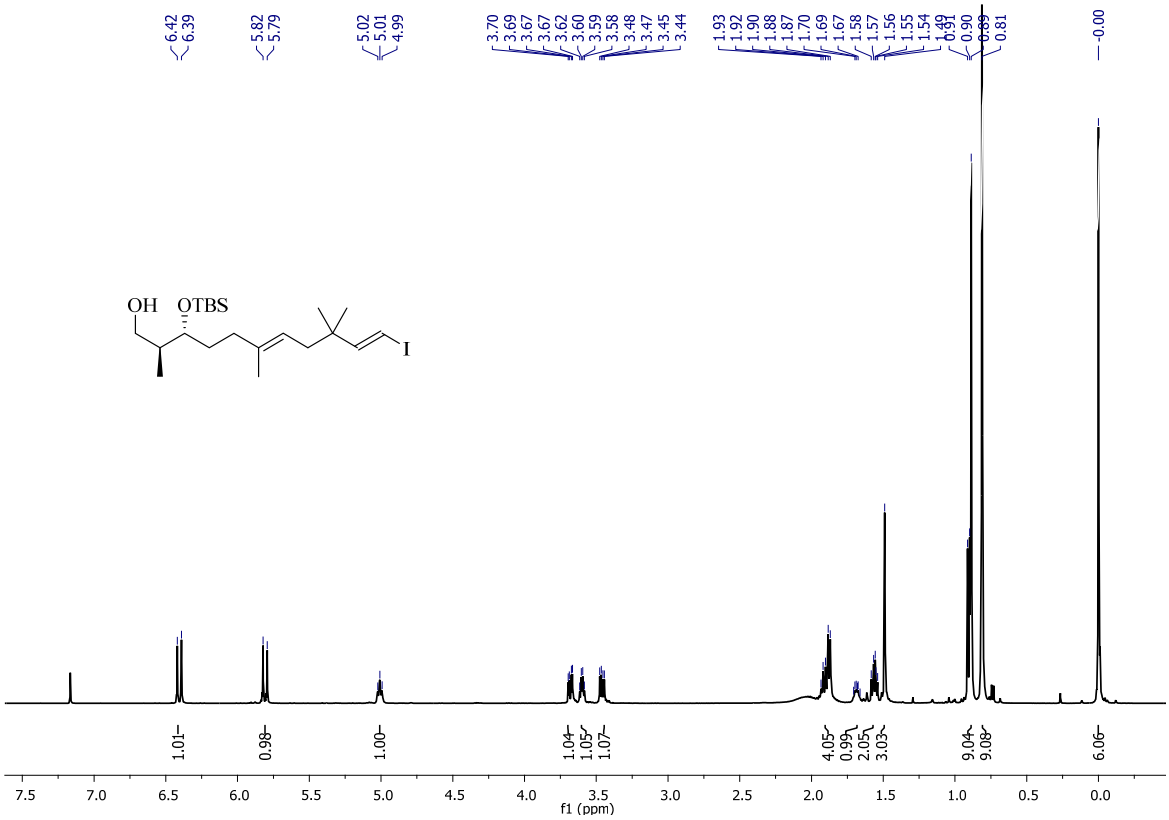
^{13}C NMR of compound 33 (125 MHz, $CDCl_3$)



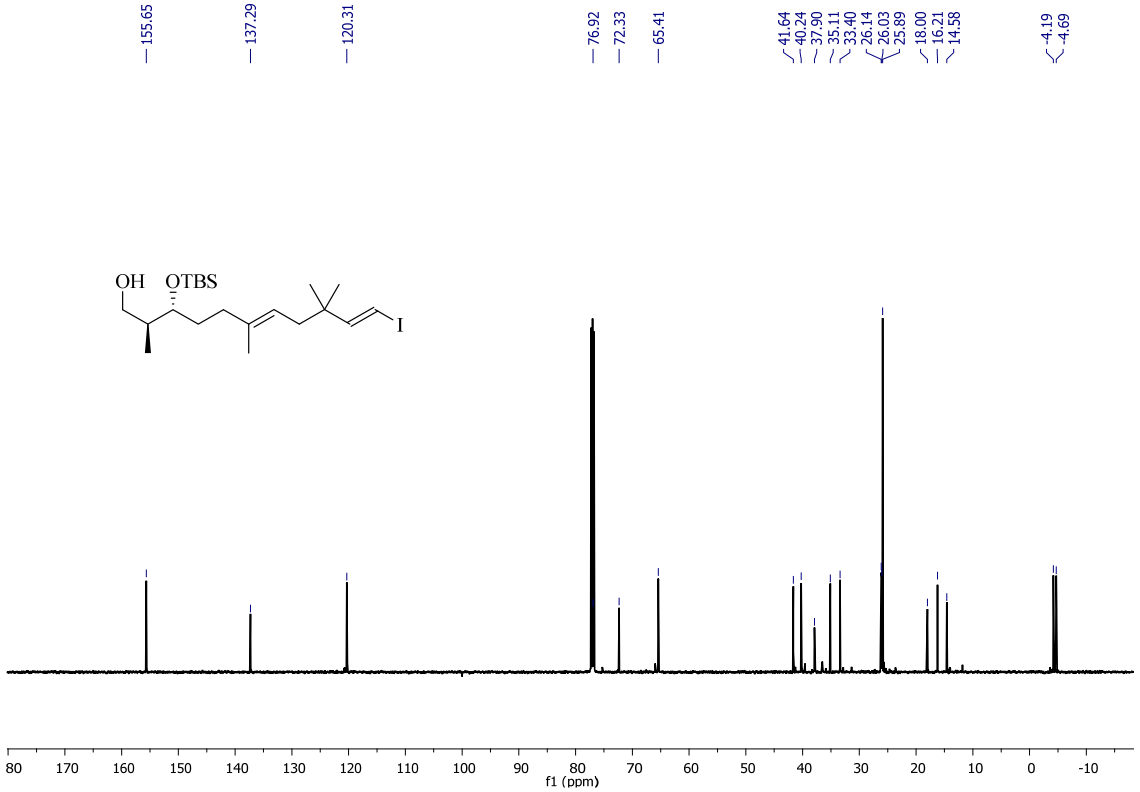
DEPT-135 of compound 33 (125 MHz, $CDCl_3$)



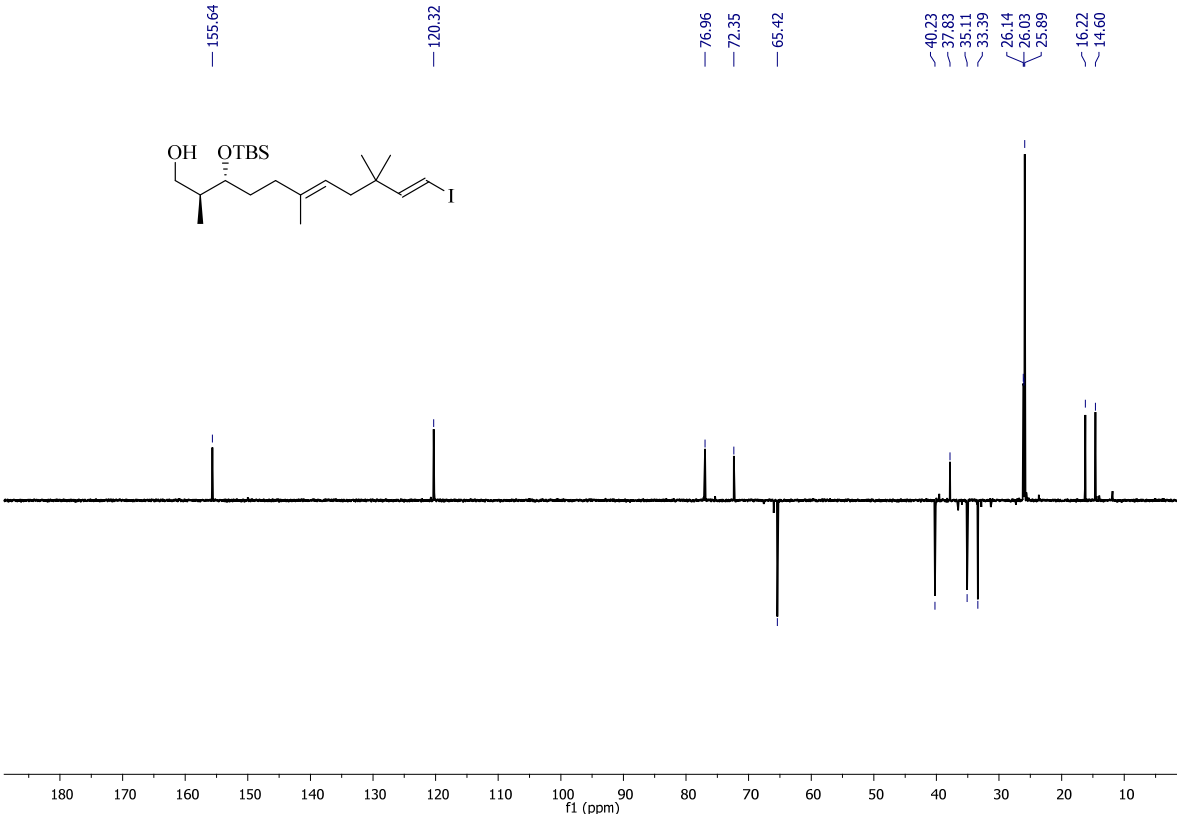
^{1}H NMR of compound 34 (500 MHz, $CDCl_3$)



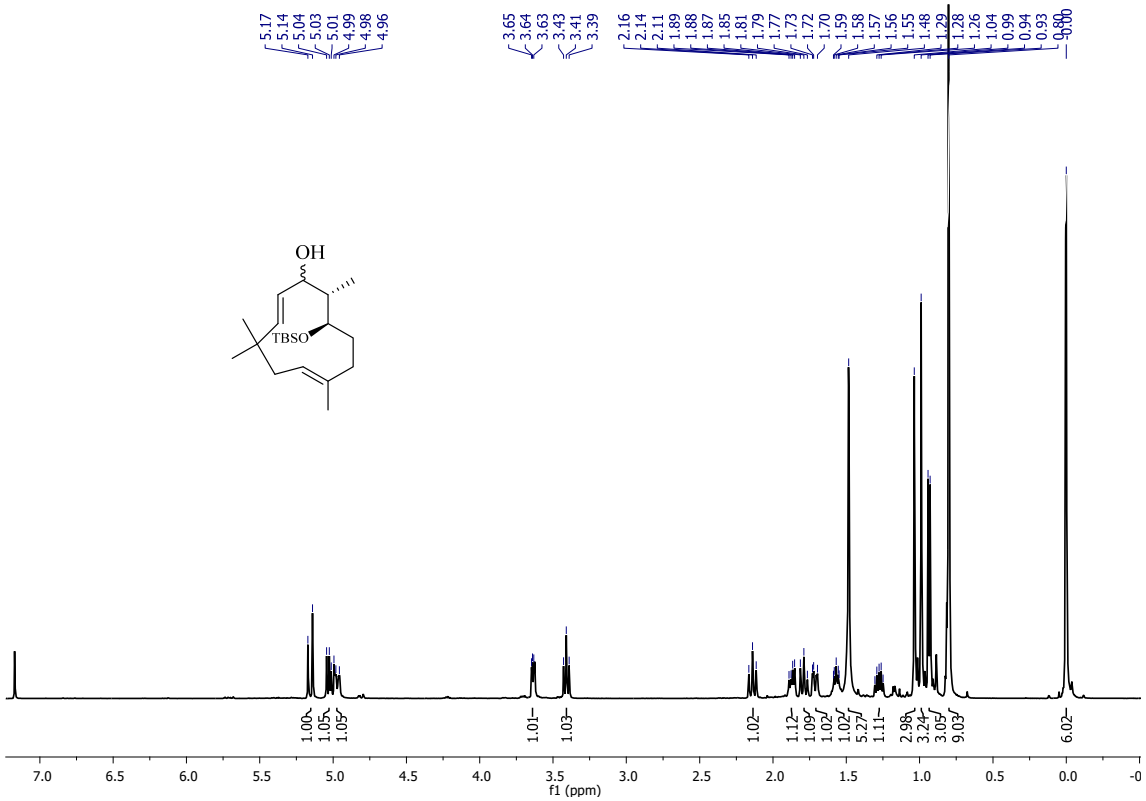
^{13}C NMR of compound 34 (125 MHz, $CDCl_3$)



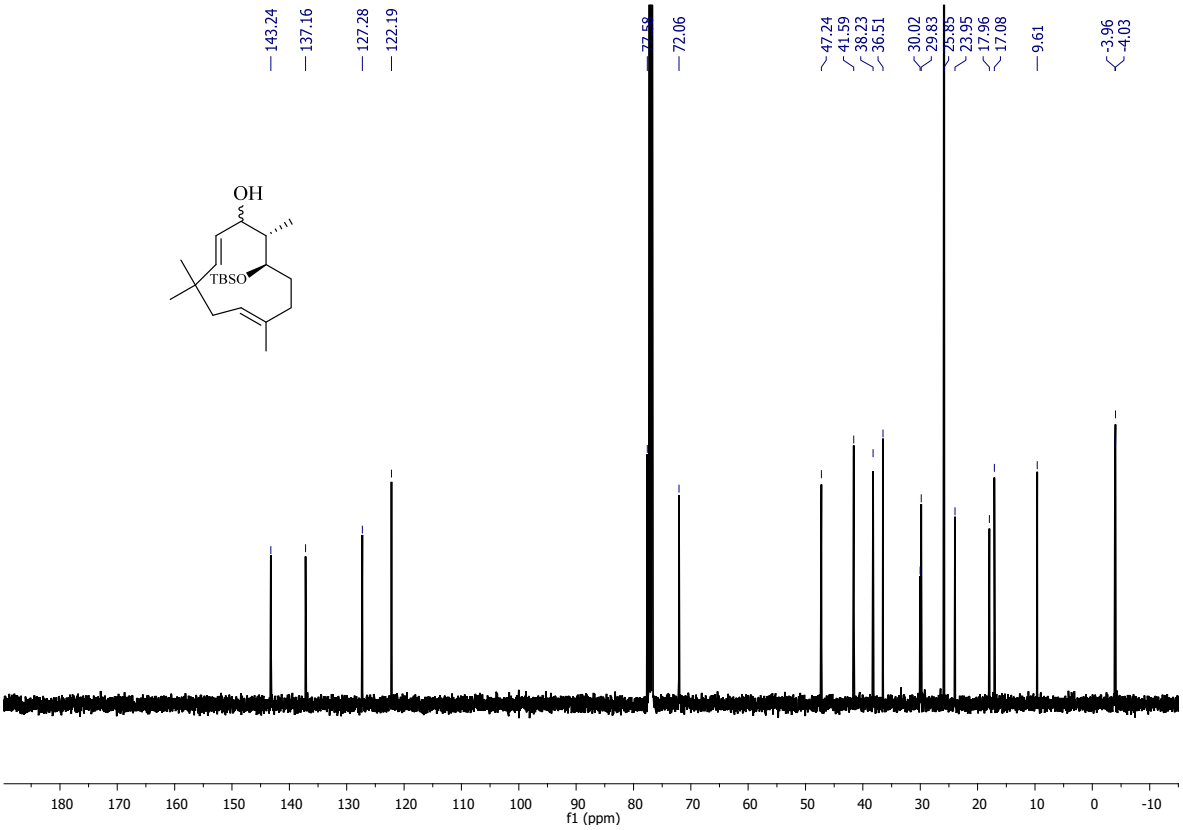
DEPT-135 of compound 34 (125 MHz, $CDCl_3$)



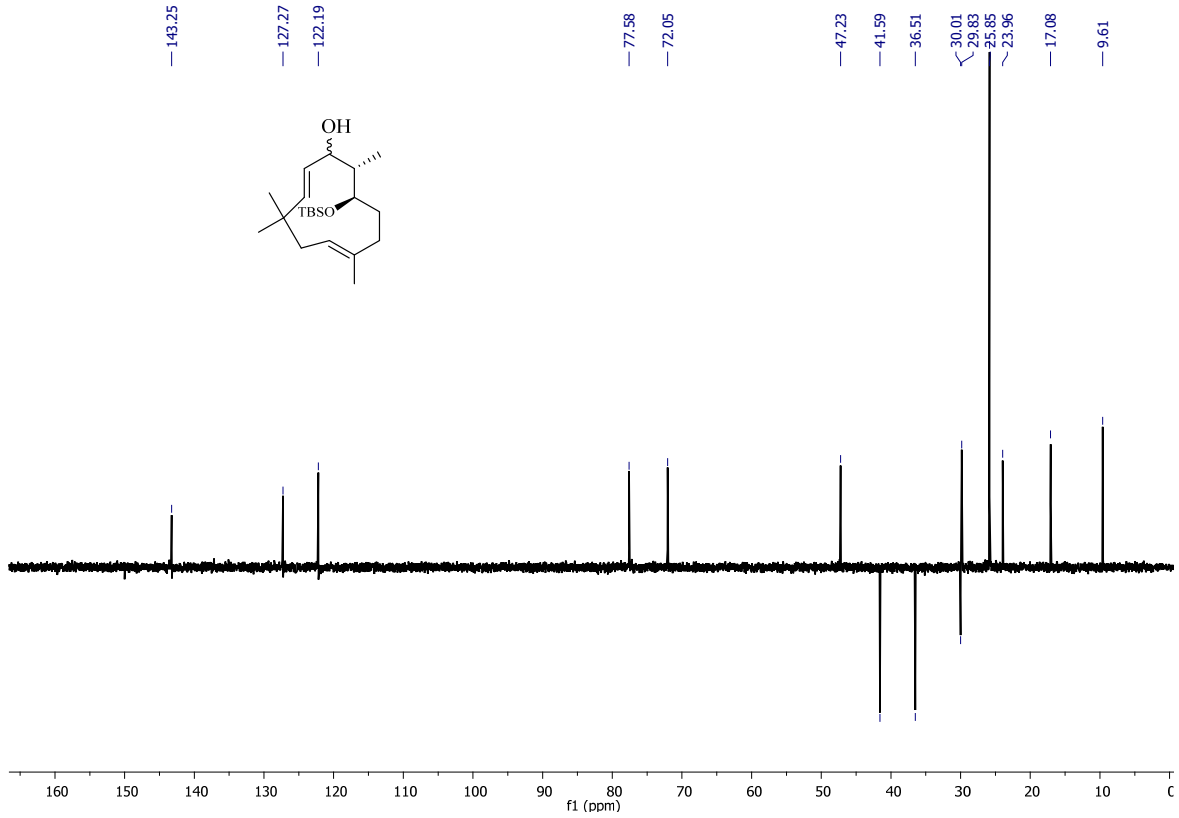
^{1}H NMR of compound 36 (500 MHz, $CDCl_3$)



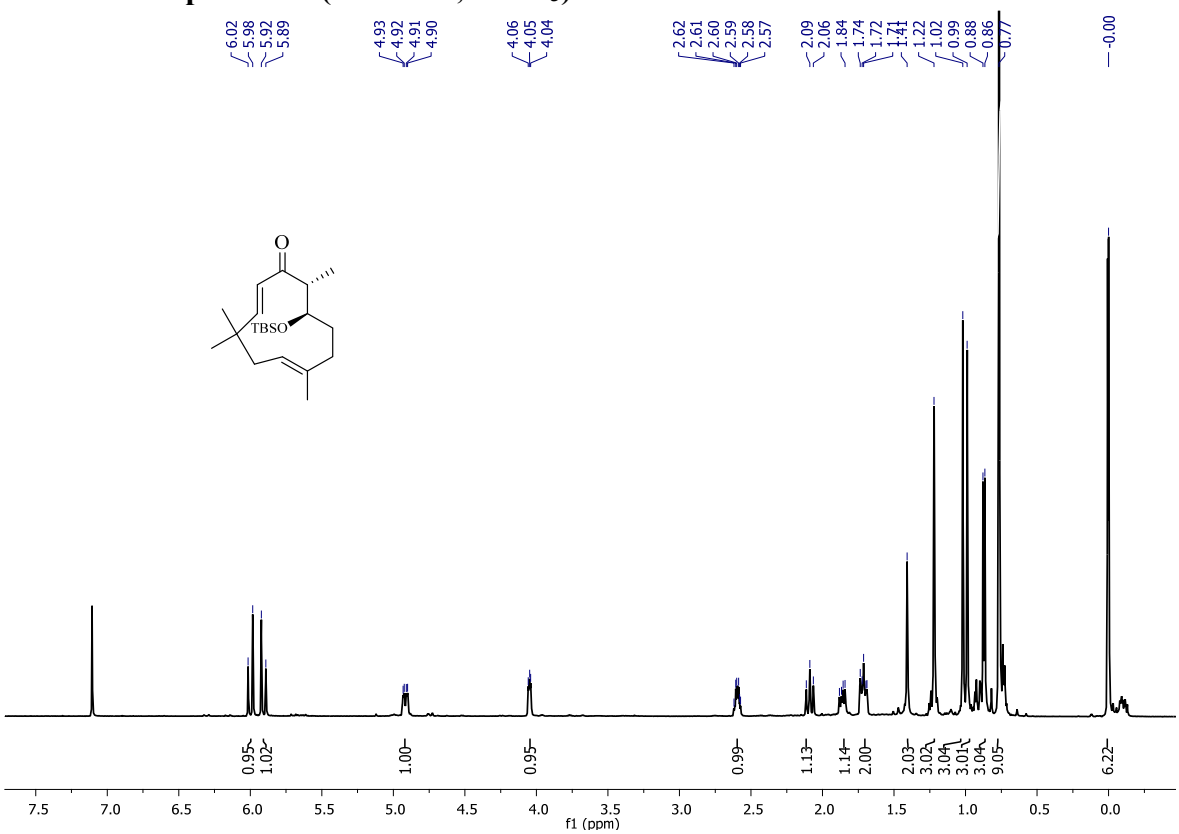
^{13}C NMR of compound 36 (125 MHz, $CDCl_3$)



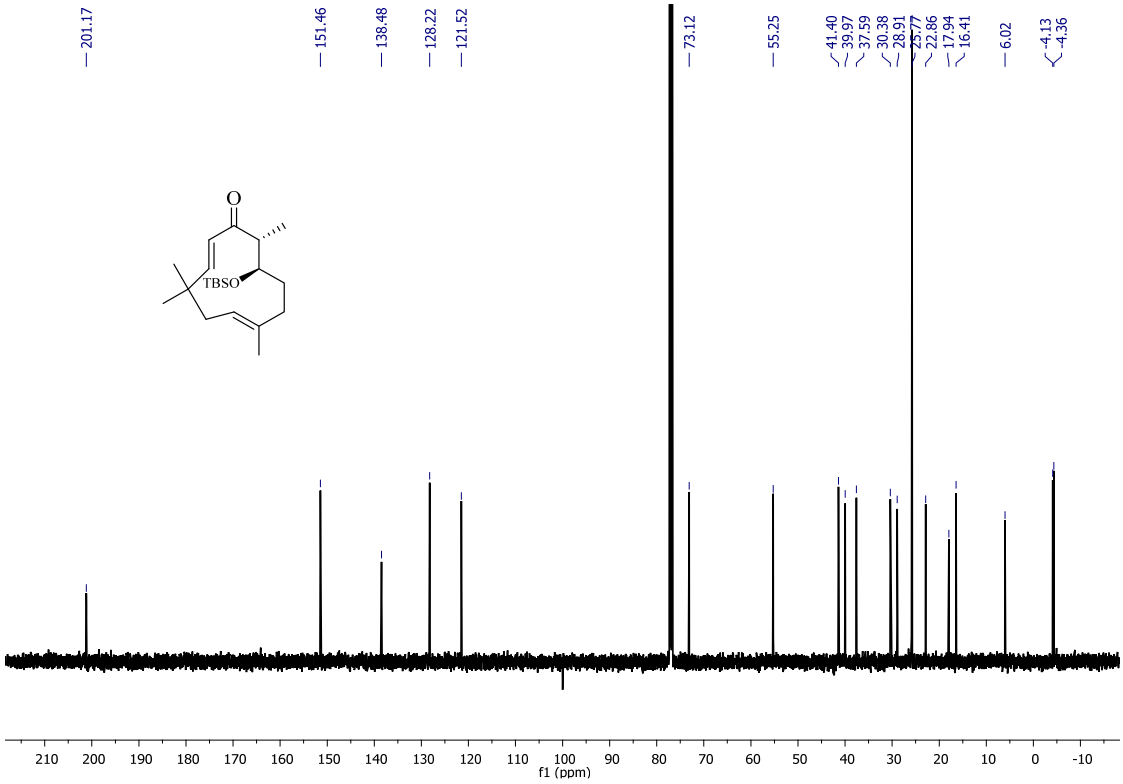
DEPT-135 of compound 36 (125 MHz, $CDCl_3$)



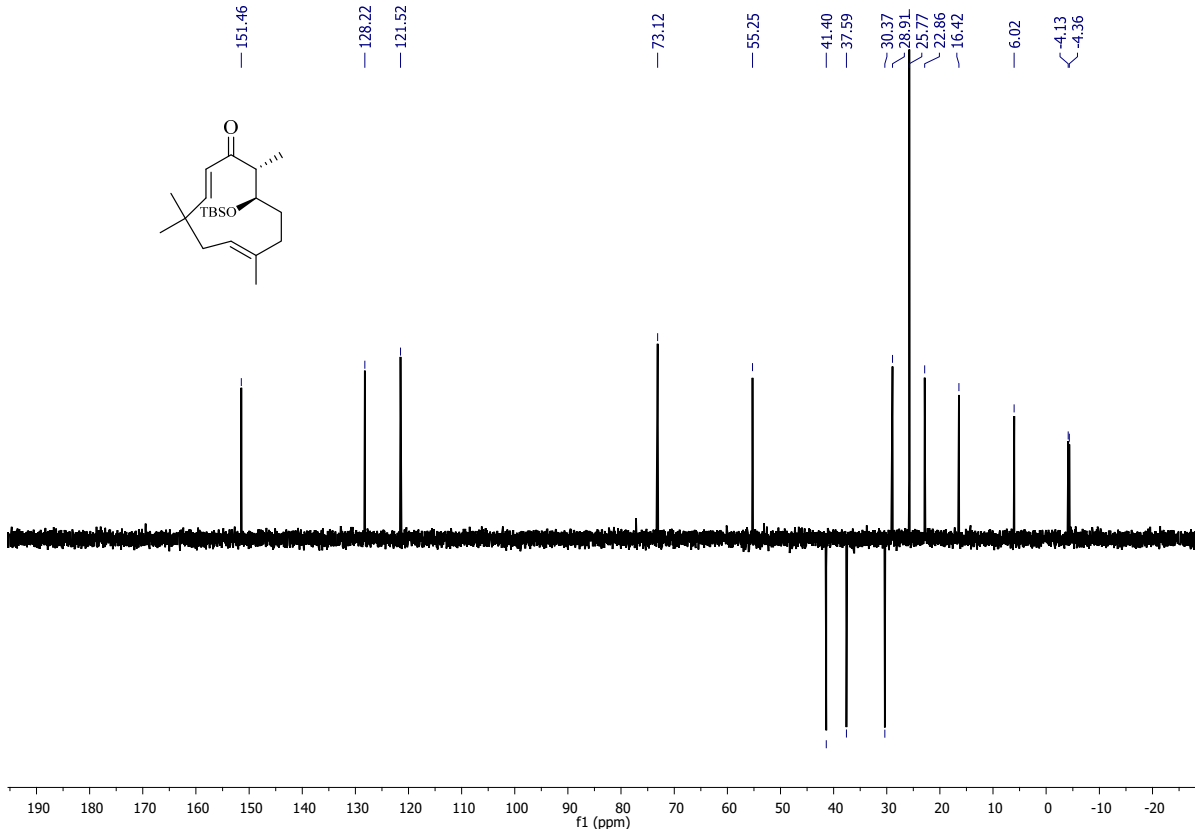
^{1}H NMR of compound 37 (500 MHz, $CDCl_3$)



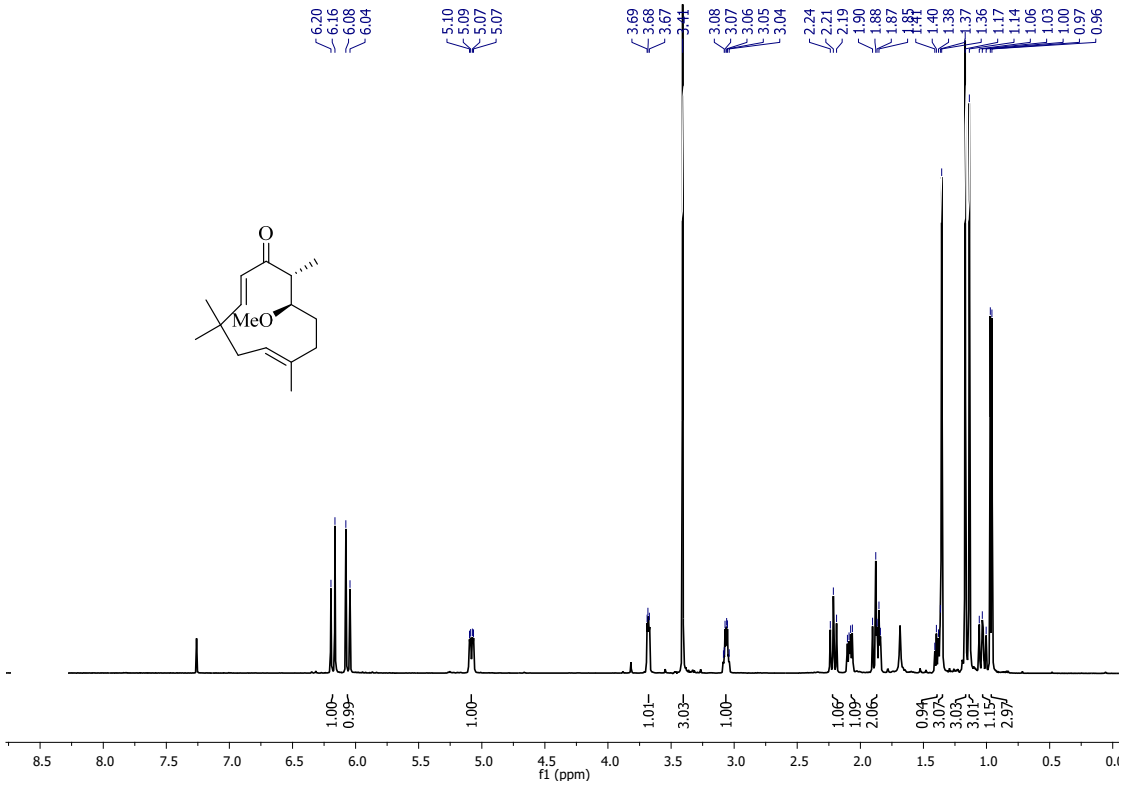
^{13}C NMR of compound 37 (125 MHz, $CDCl_3$)



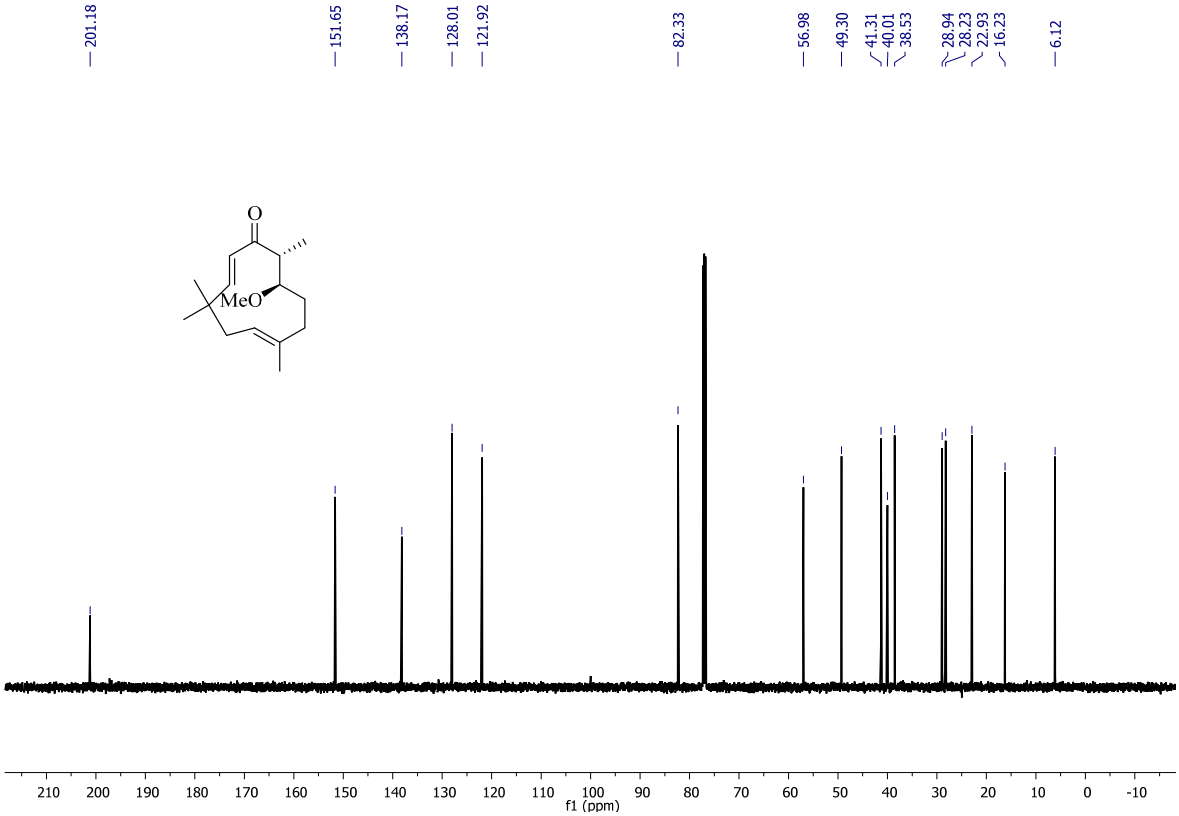
DEPT-135 of compound 37 (125 MHz, $CDCl_3$)



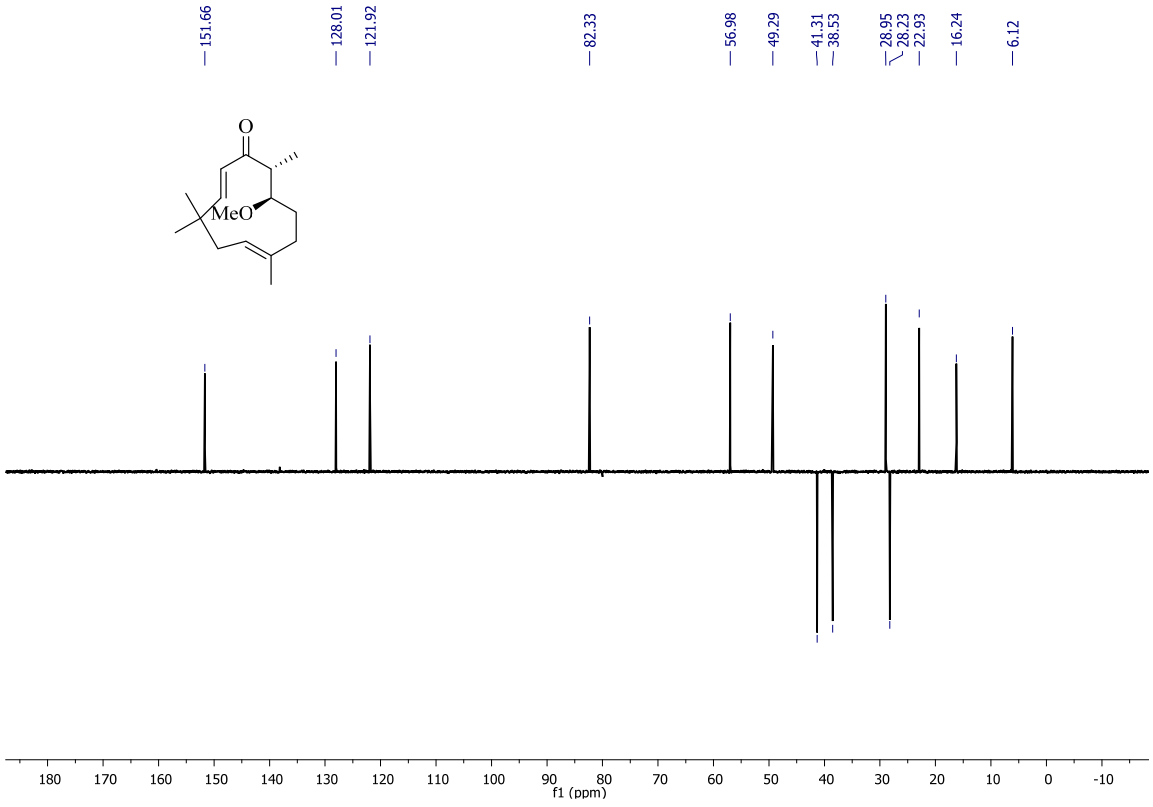
^{1}H NMR of compound 38 (500 MHz, $CDCl_3$)



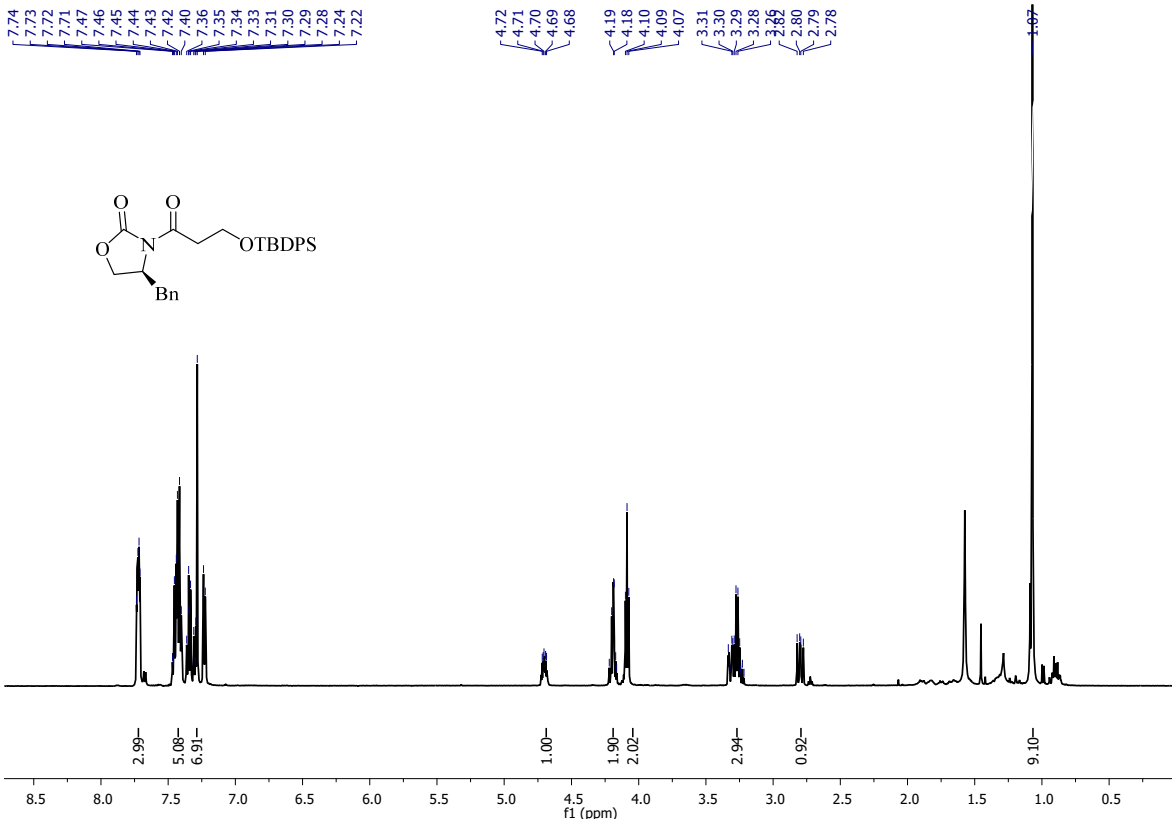
^{13}C NMR of compound 38 (125 MHz, $CDCl_3$)



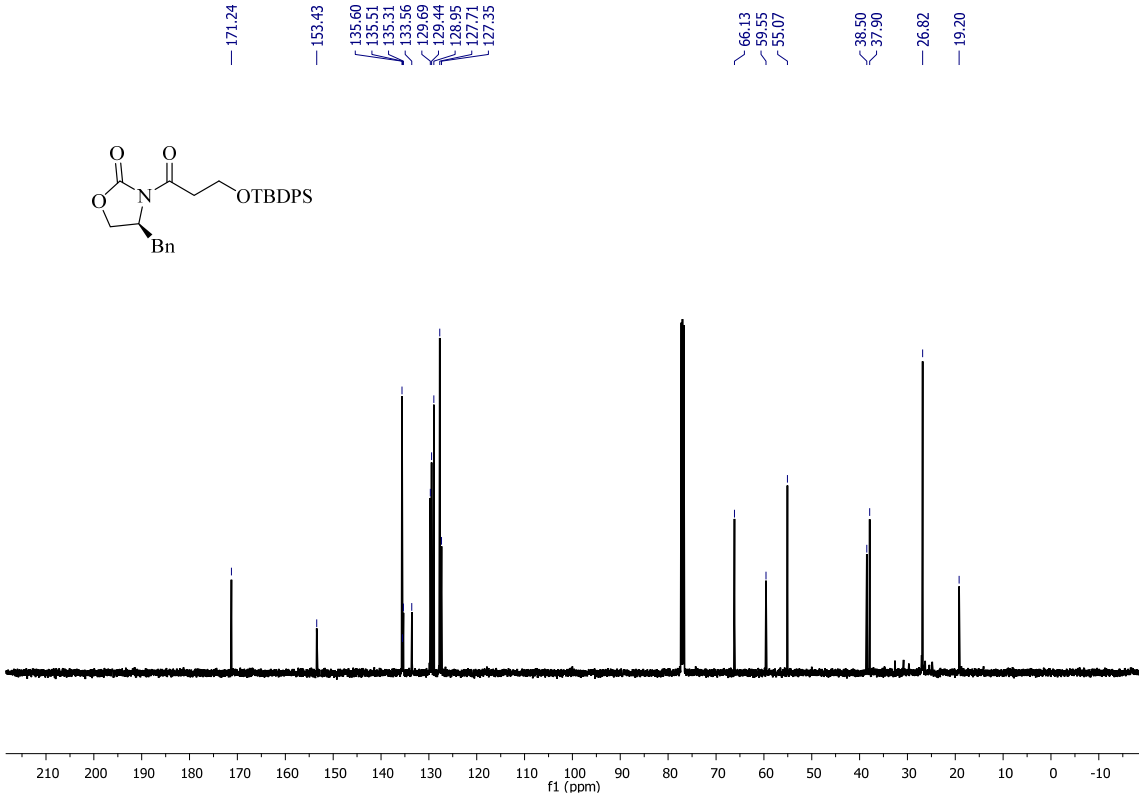
DEPT-135 of compound 38 (125 MHz, $CDCl_3$)



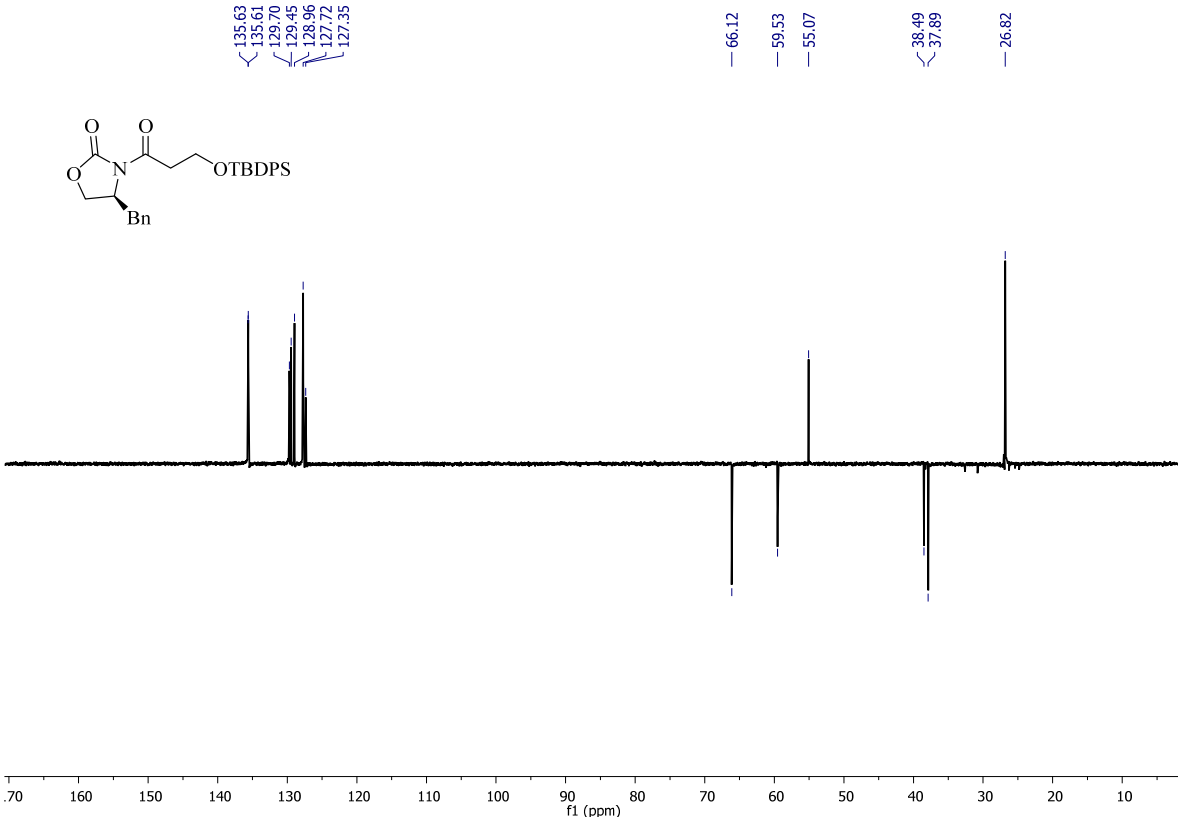
^{1}H NMR of compound 39 (500 MHz, $CDCl_3$)



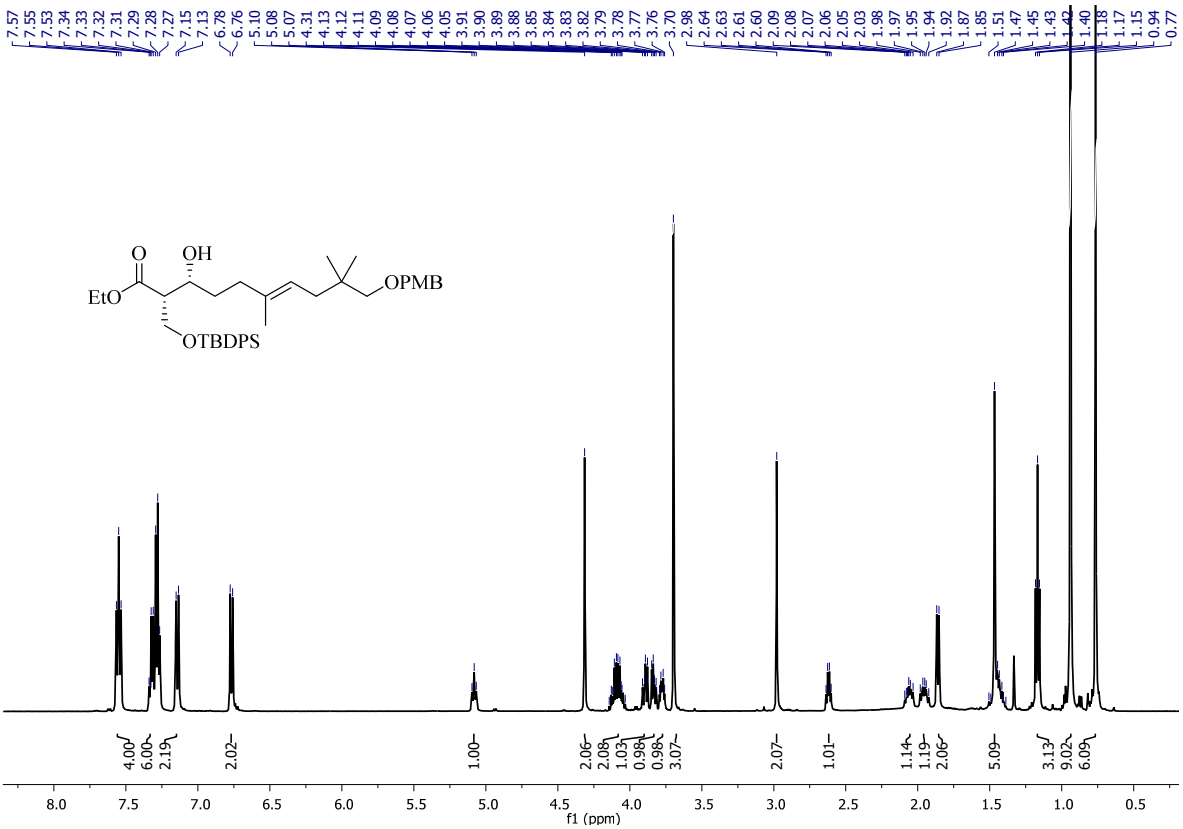
^{13}C NMR of compound 39 (125 MHz, $CDCl_3$)



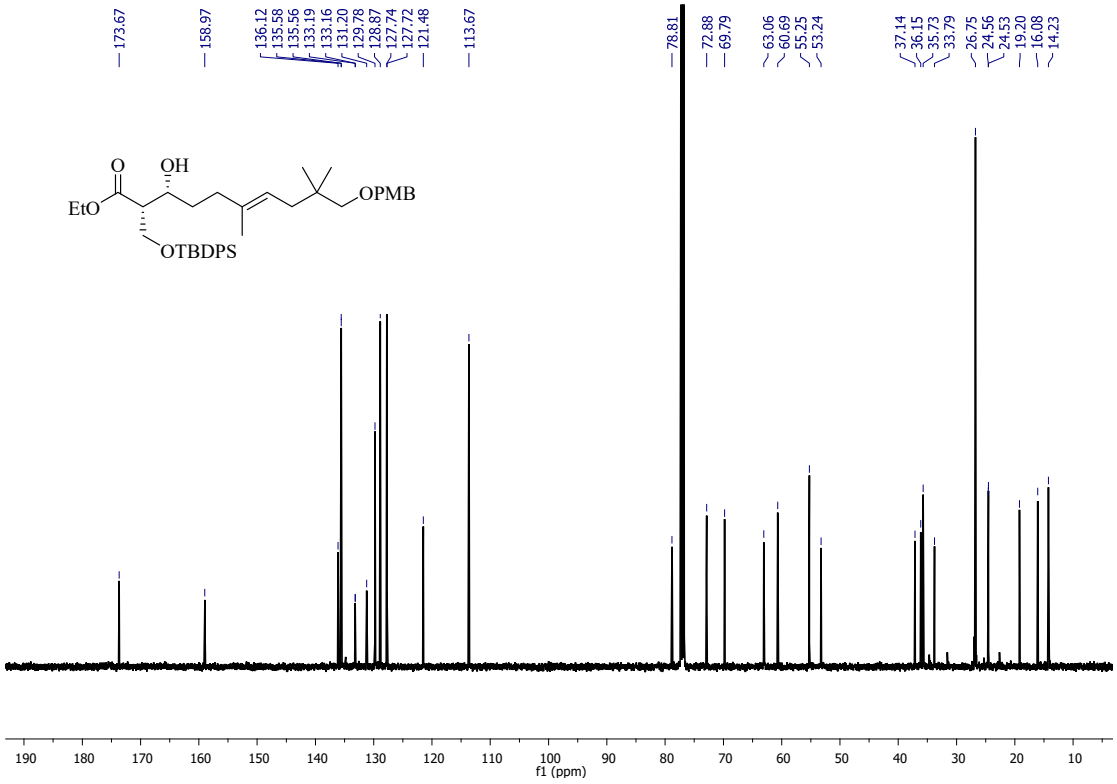
DEPT-135 of compound 39 (125 MHz, $CDCl_3$)



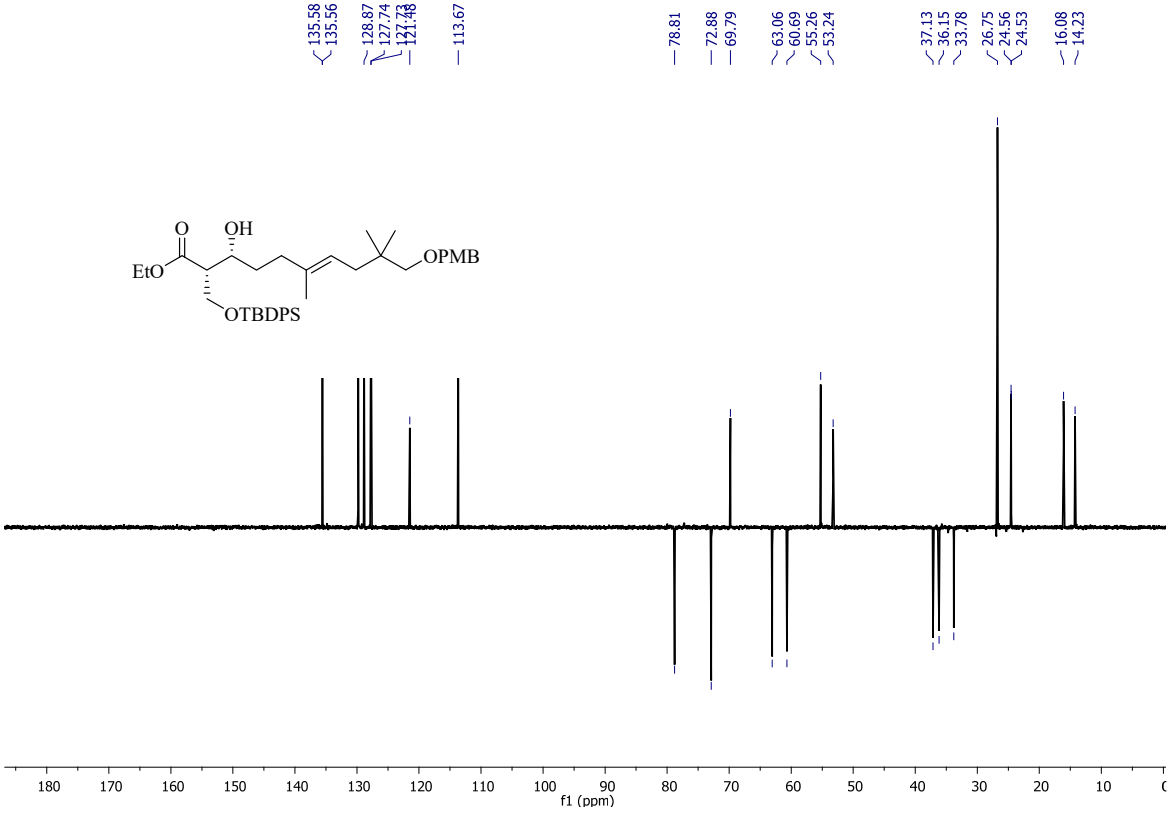
^{1}H NMR of compound 41a (500 MHz, $CDCl_3$)



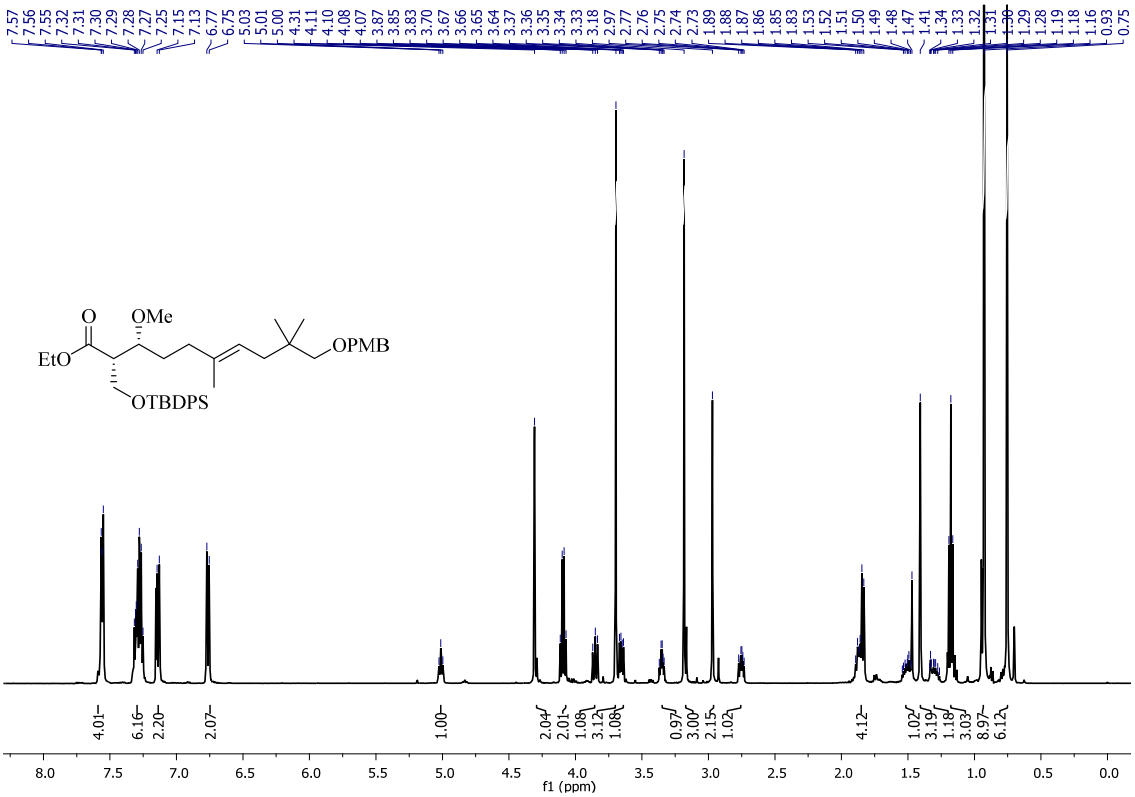
^{13}C NMR of compound 41a (125 MHz, $CDCl_3$)



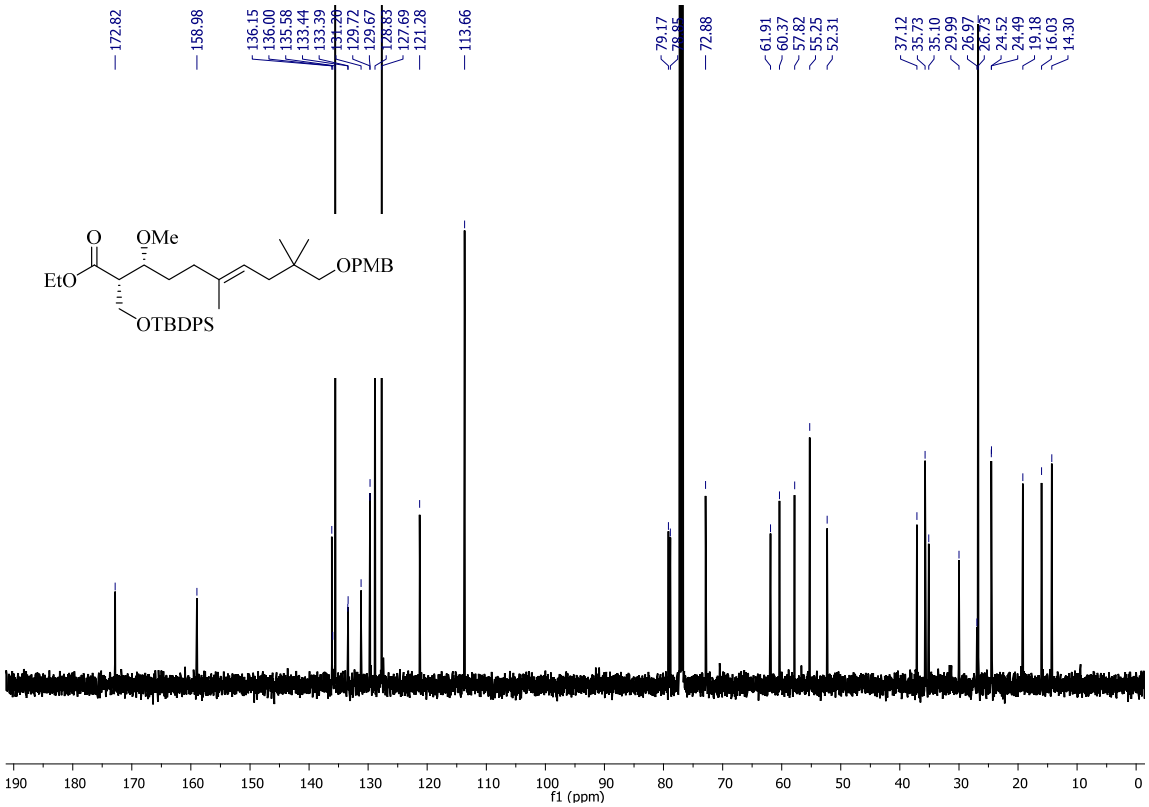
DEPT-135 of compound 41a (125 MHz, $CDCl_3$)



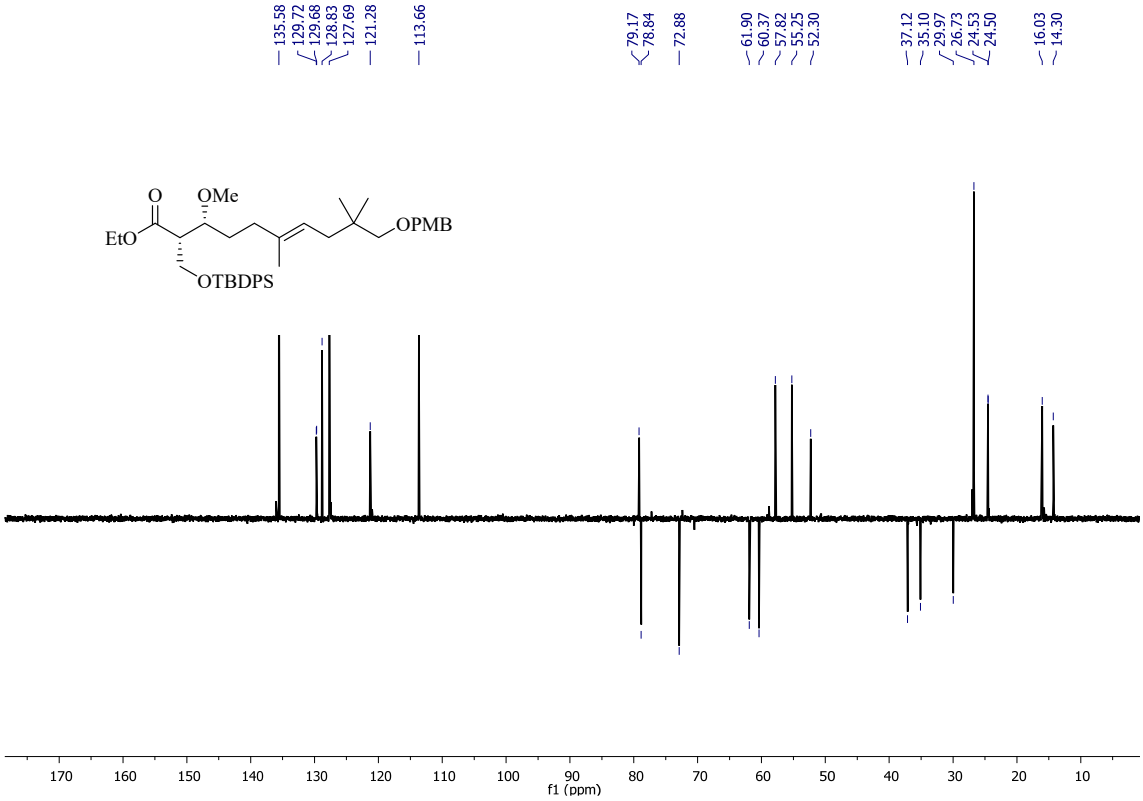
^{1}H NMR of compound 42a (500 MHz, $CDCl_3$)



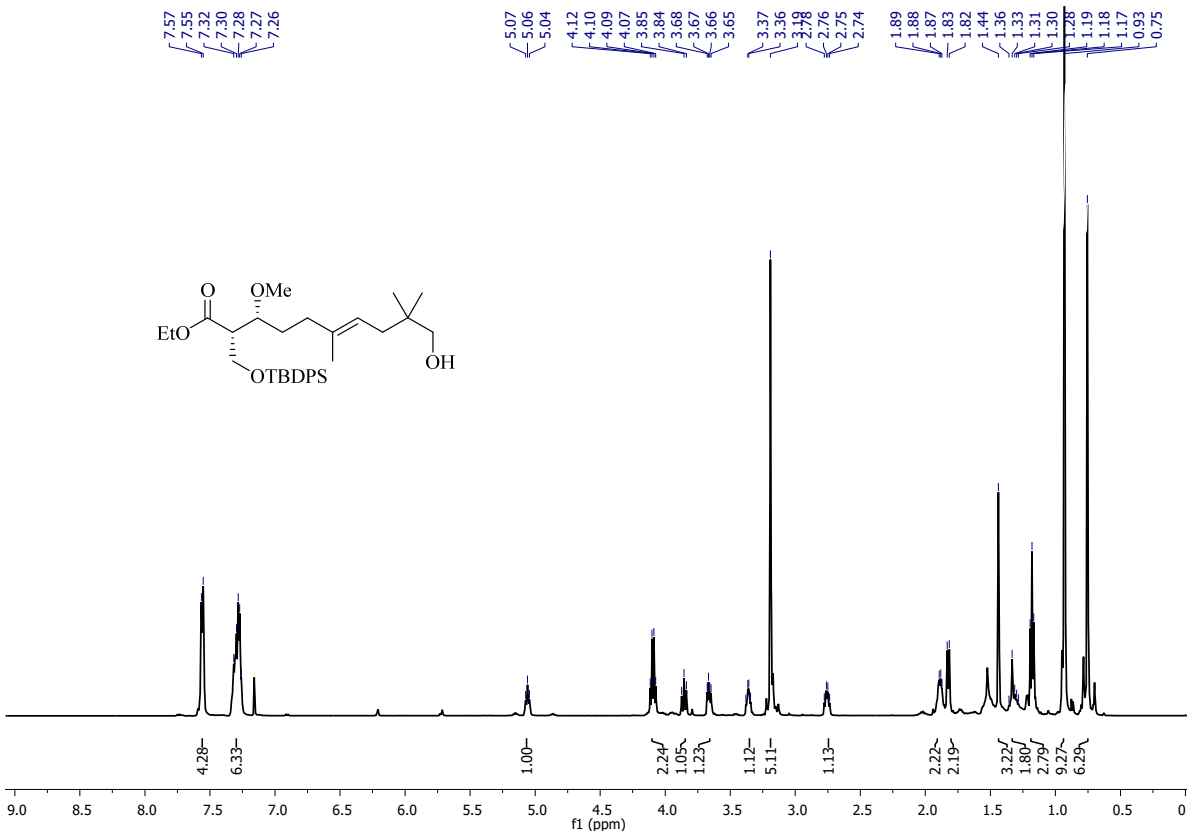
^{13}C NMR of compound 42a (125 MHz, $CDCl_3$)



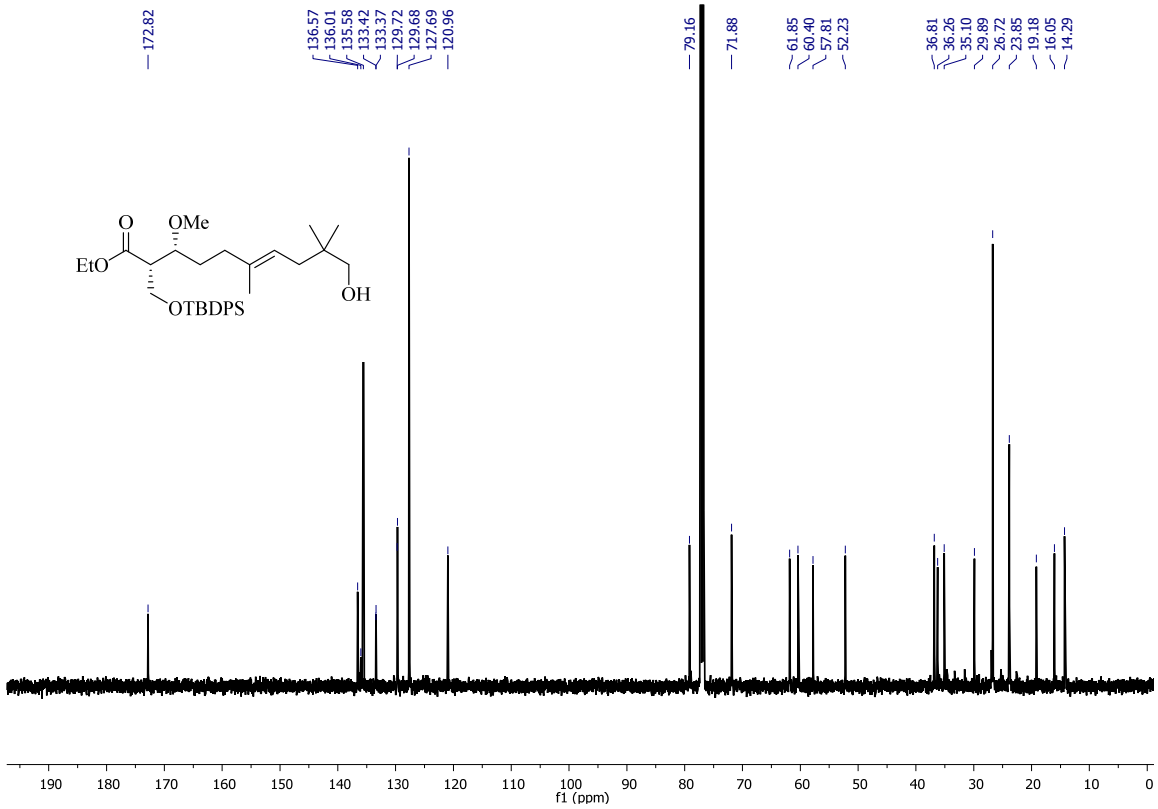
DEPT-135 of compound 42a (125 MHz, $CDCl_3$)



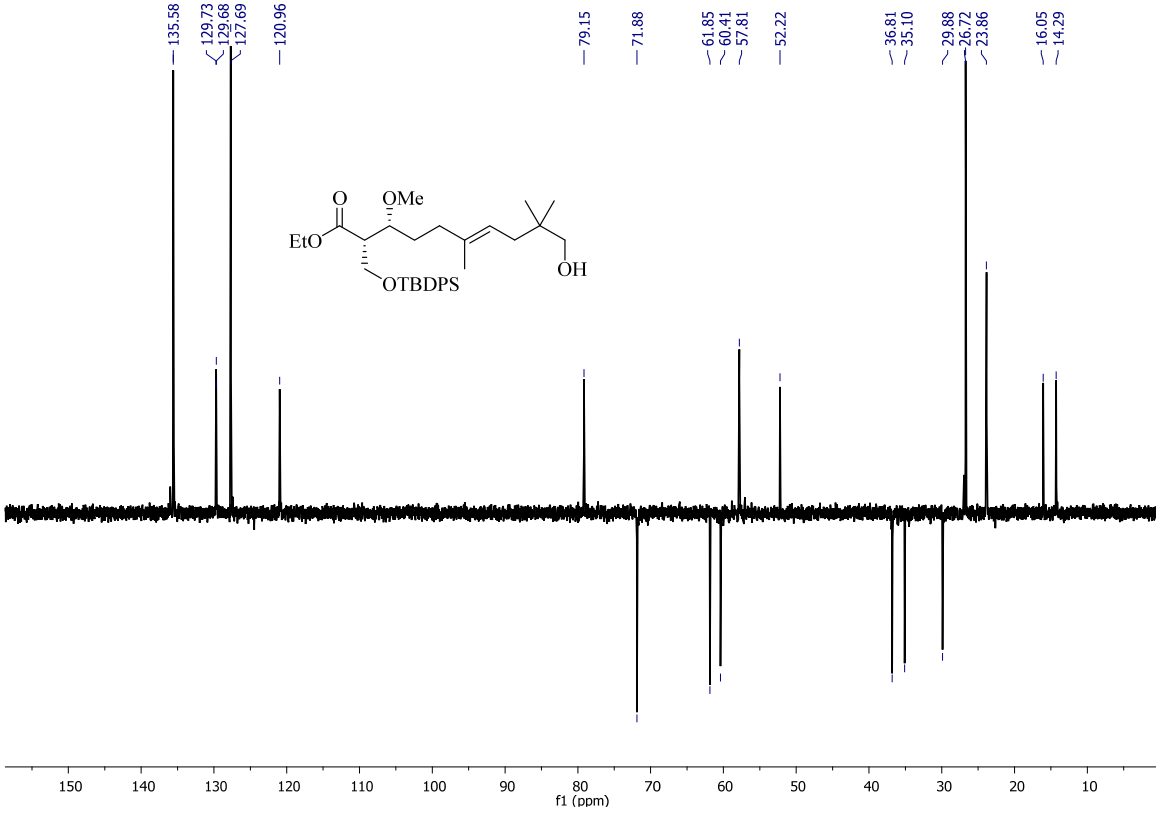
^{1}H NMR of compound 43a (500 MHz, $CDCl_3$)



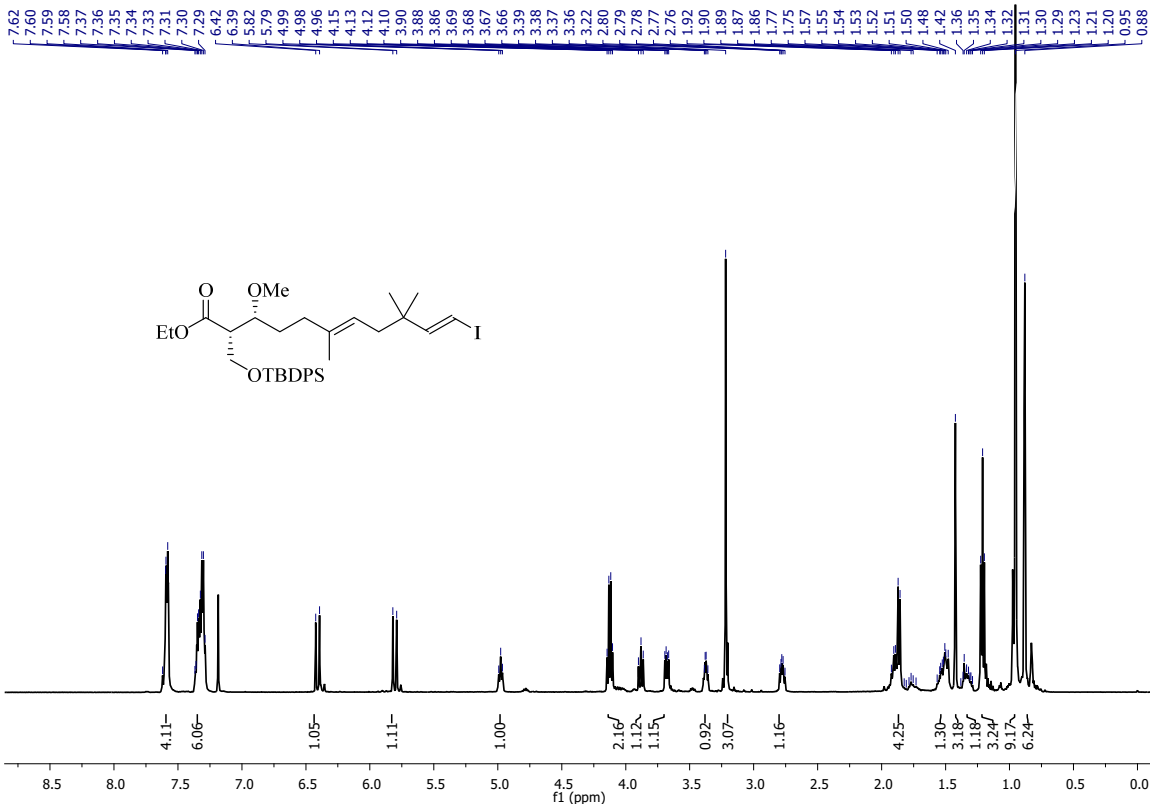
^{13}C NMR of compound 43a (125 MHz, $CDCl_3$)



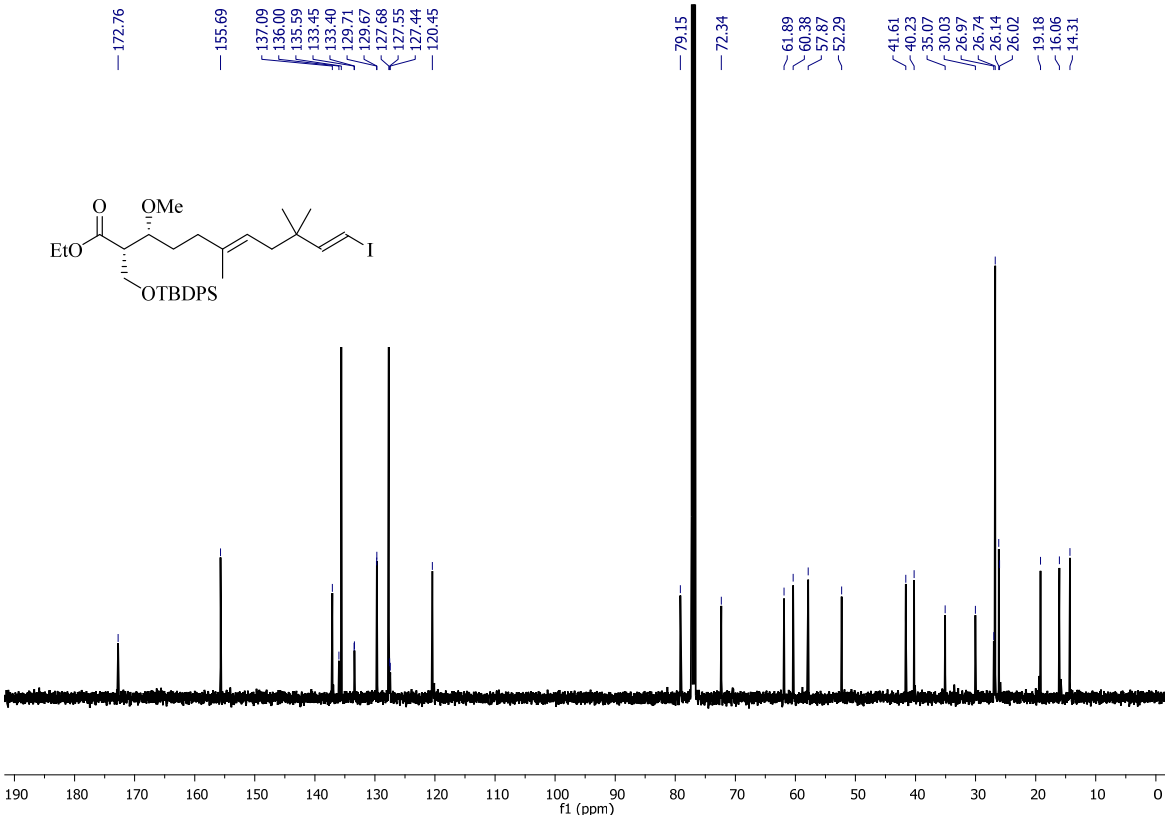
DEPT-135 of compound 43a (125 MHz, $CDCl_3$)



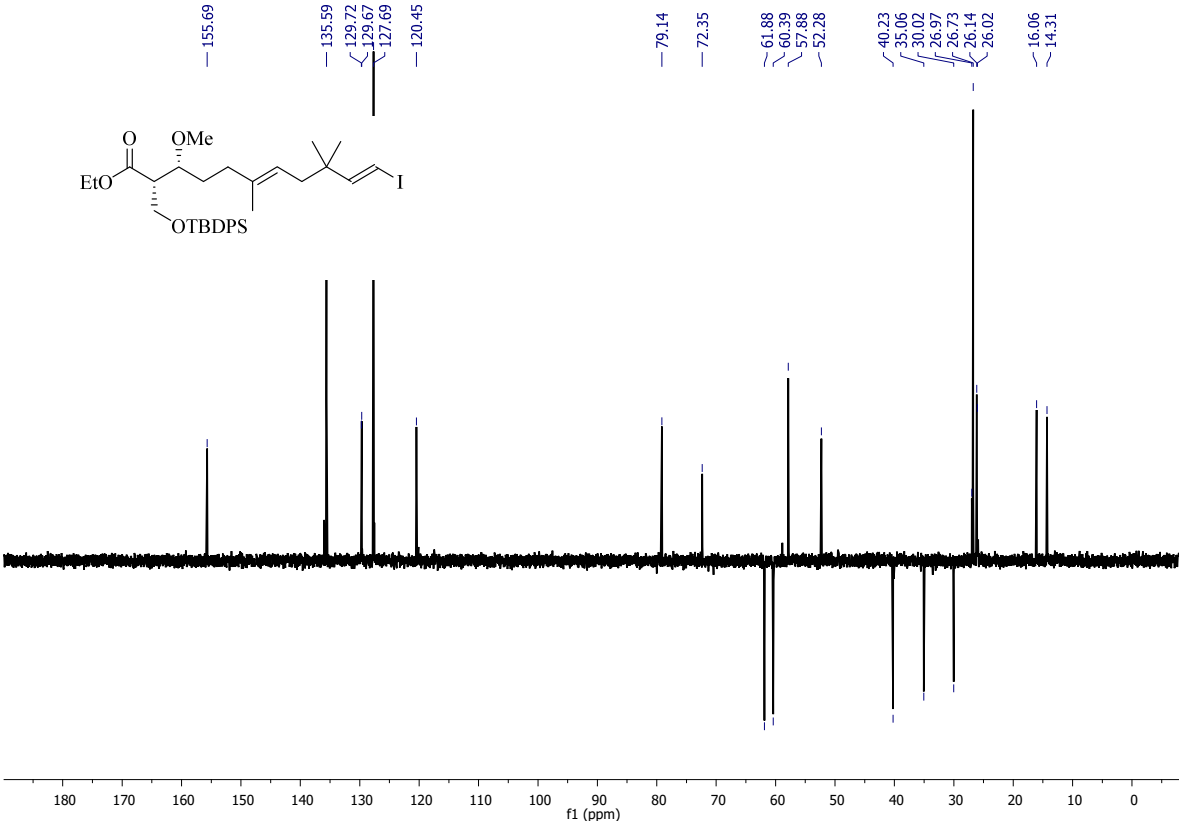
^{1}H NMR of compound 45a (500 MHz, $CDCl_3$)



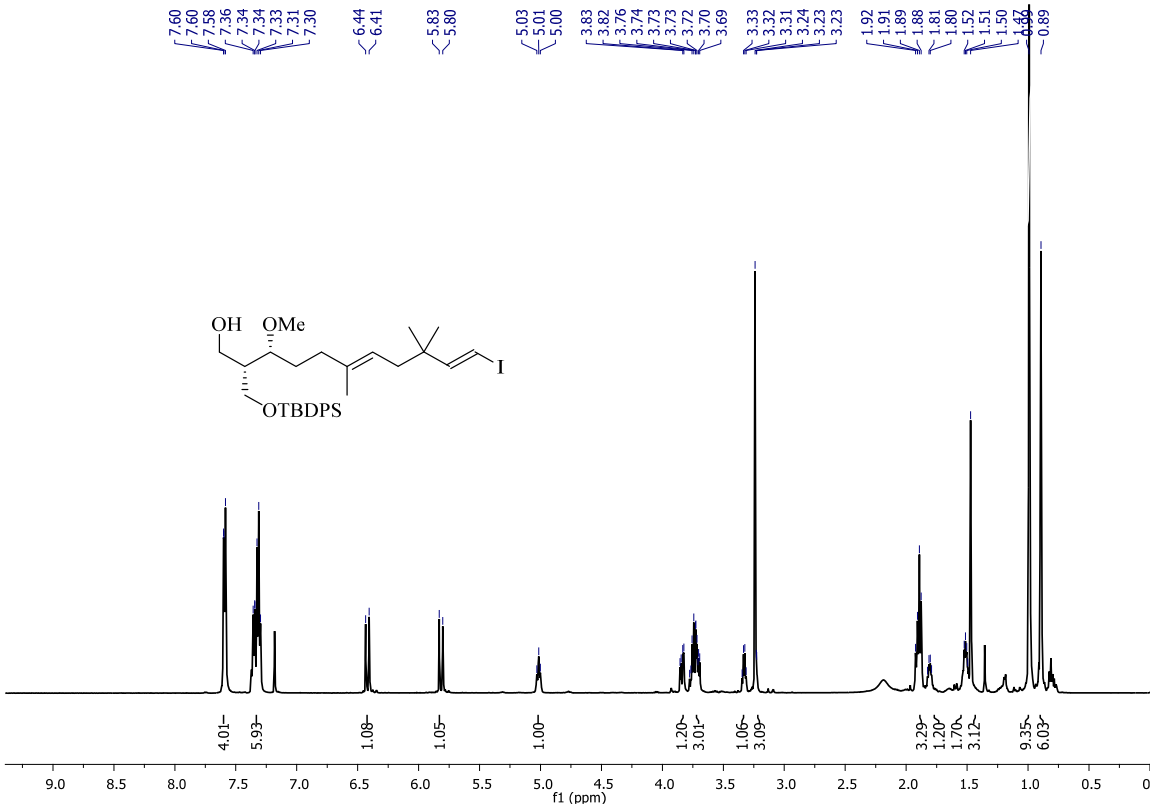
^{13}C NMR of compound 45a (125 MHz, $CDCl_3$)



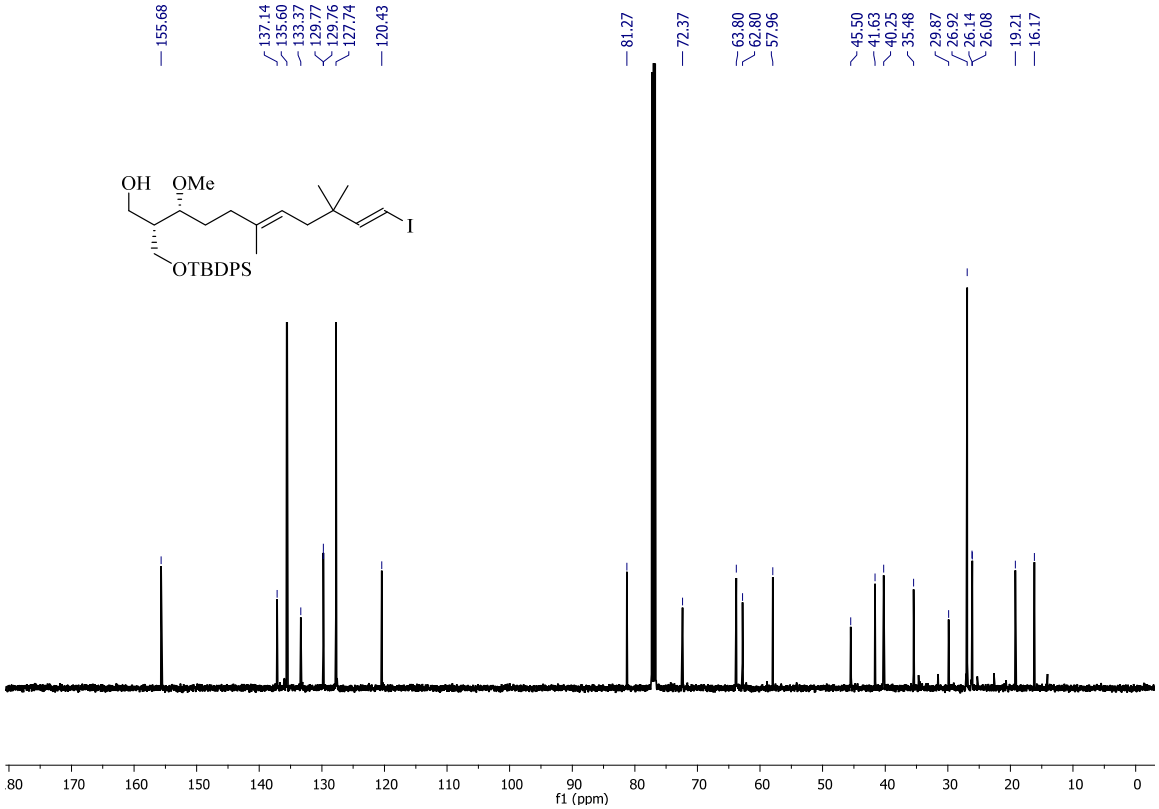
DEPT-135 of compound 45a (125 MHz, $CDCl_3$)



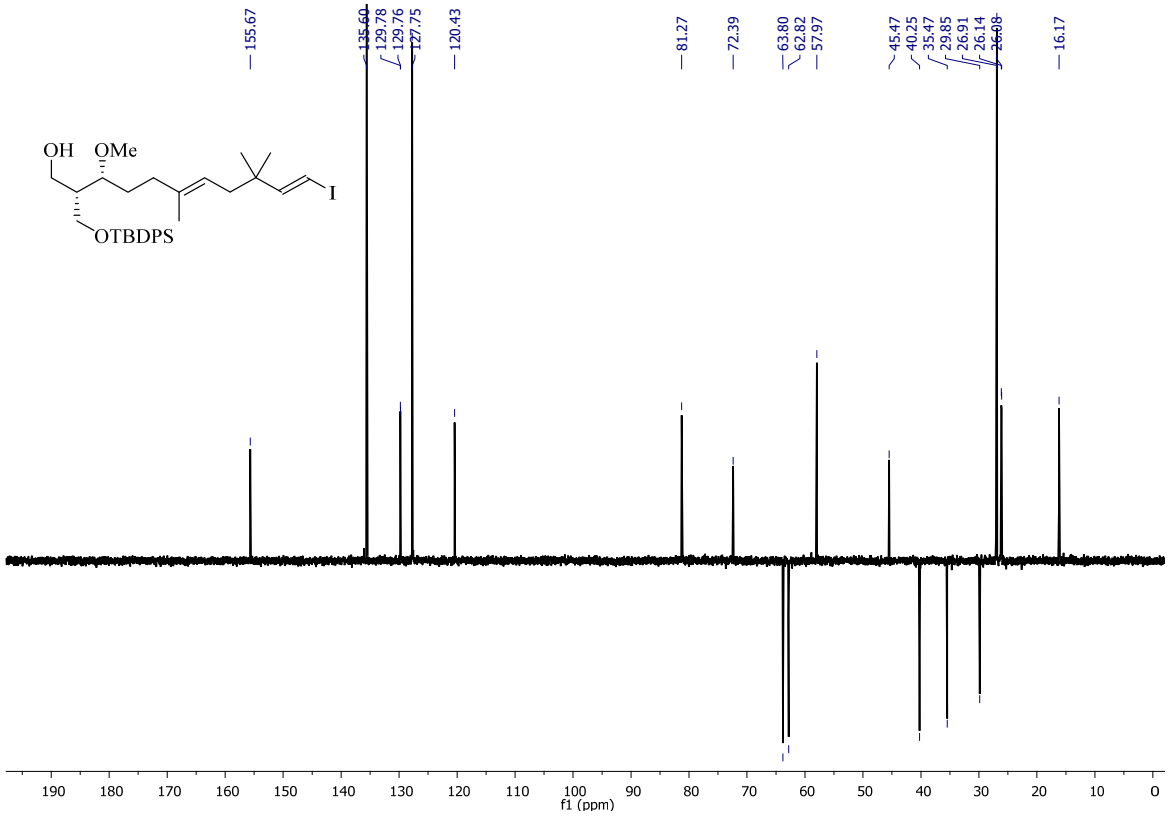
^{1}H NMR of compound 46a (500 MHz, $CDCl_3$)



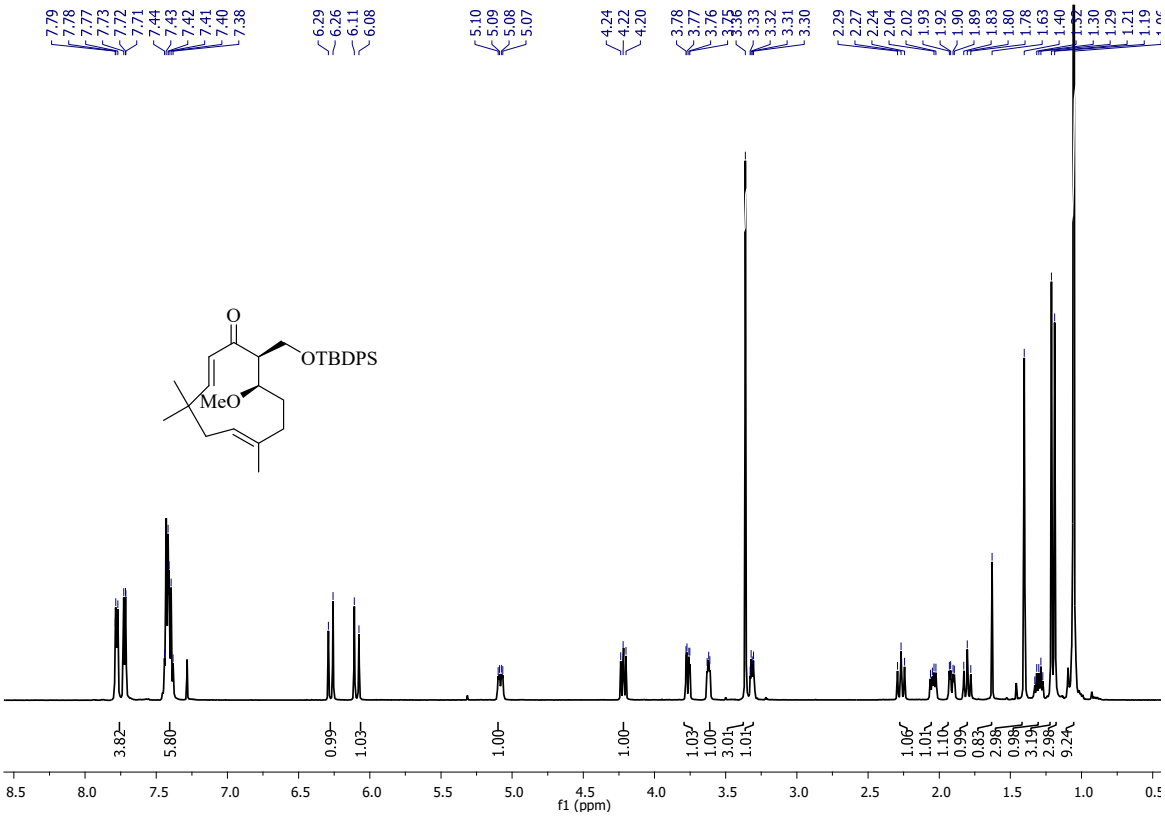
^{13}C NMR of compound 46a (125 MHz, $CDCl_3$)



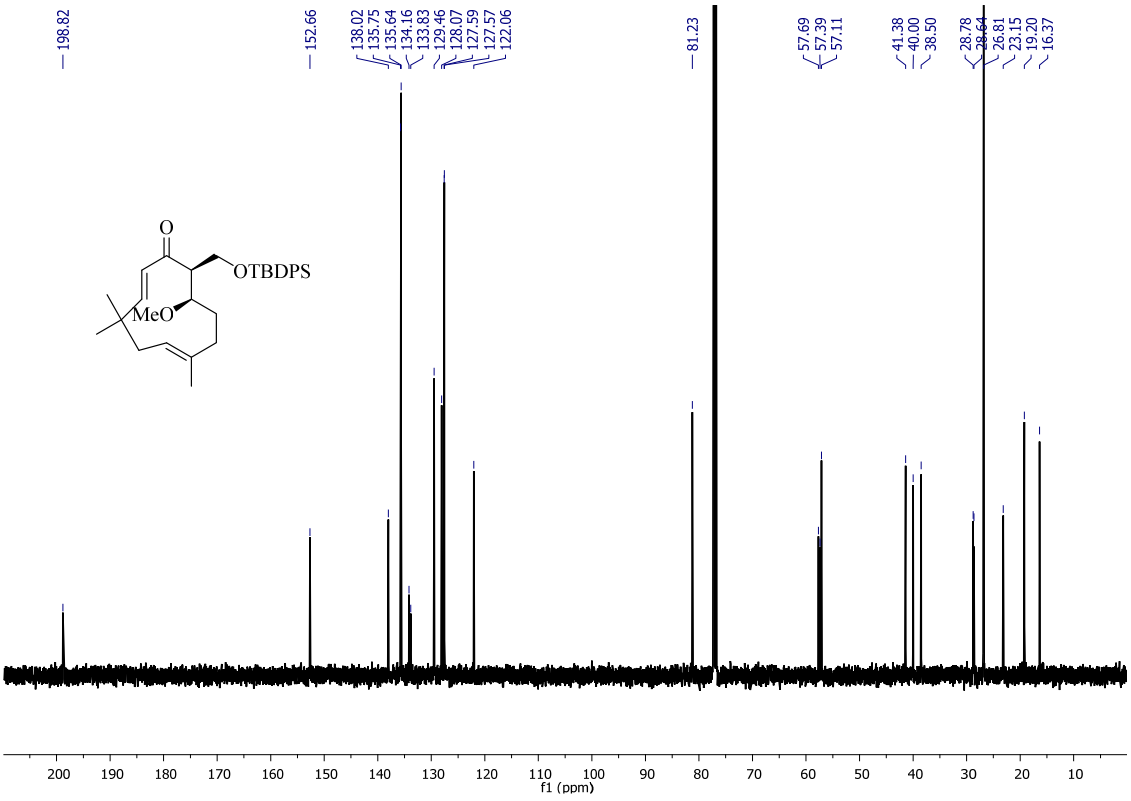
DEPT-135 of compound 46a (125 MHz, $CDCl_3$)



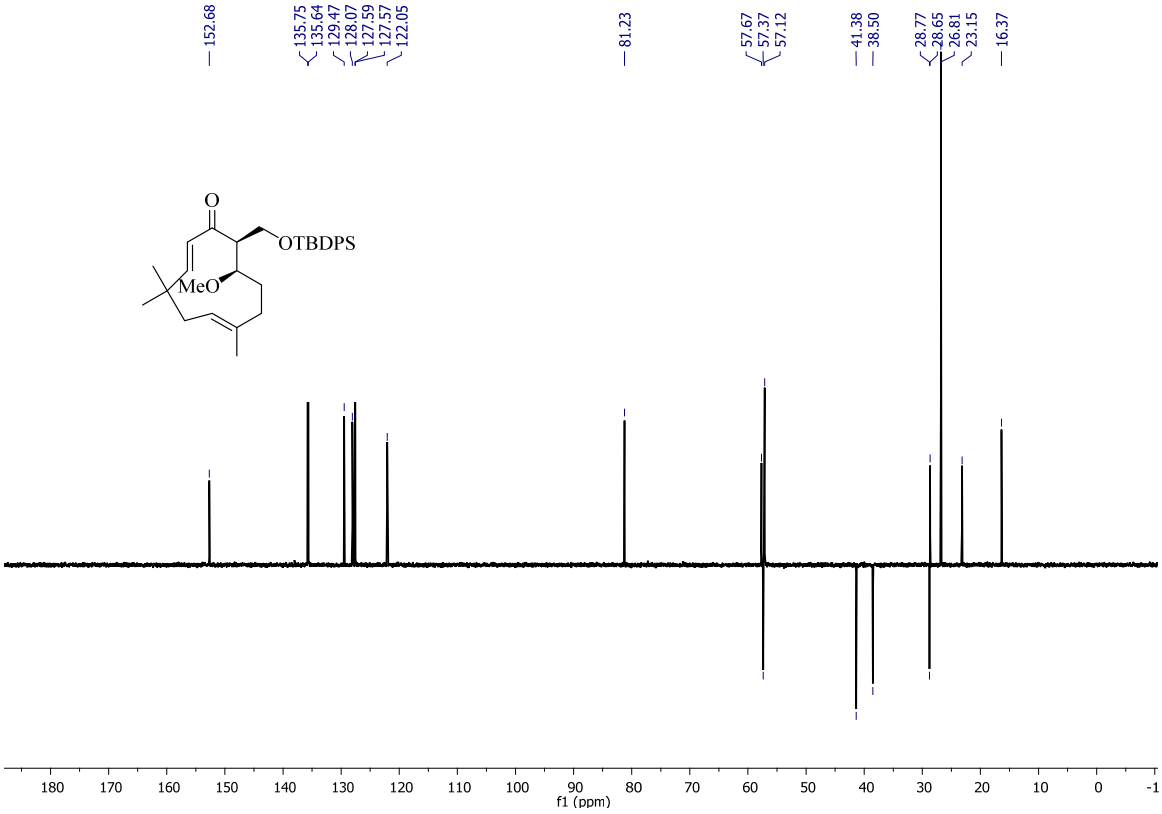
^{1}H NMR of compound 47a (500 MHz, $CDCl_3$)



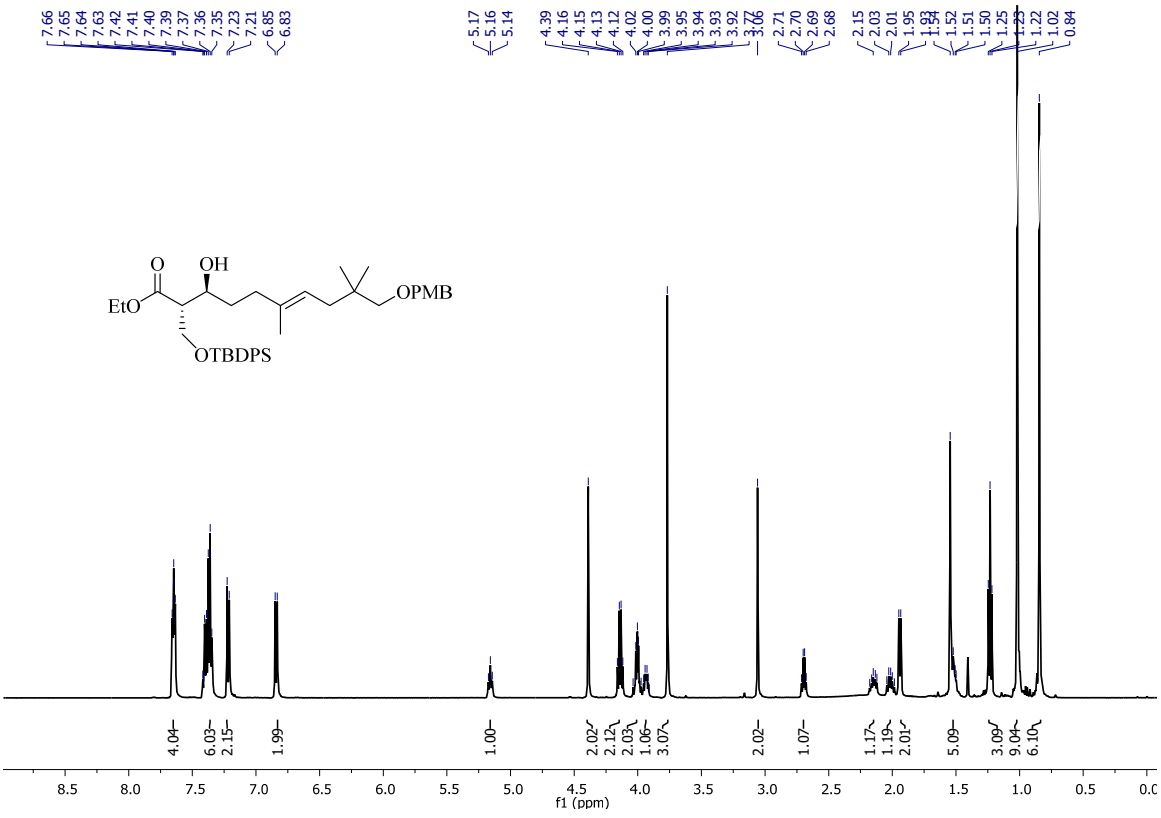
^{13}C NMR of compound 47a (125 MHz, $CDCl_3$)



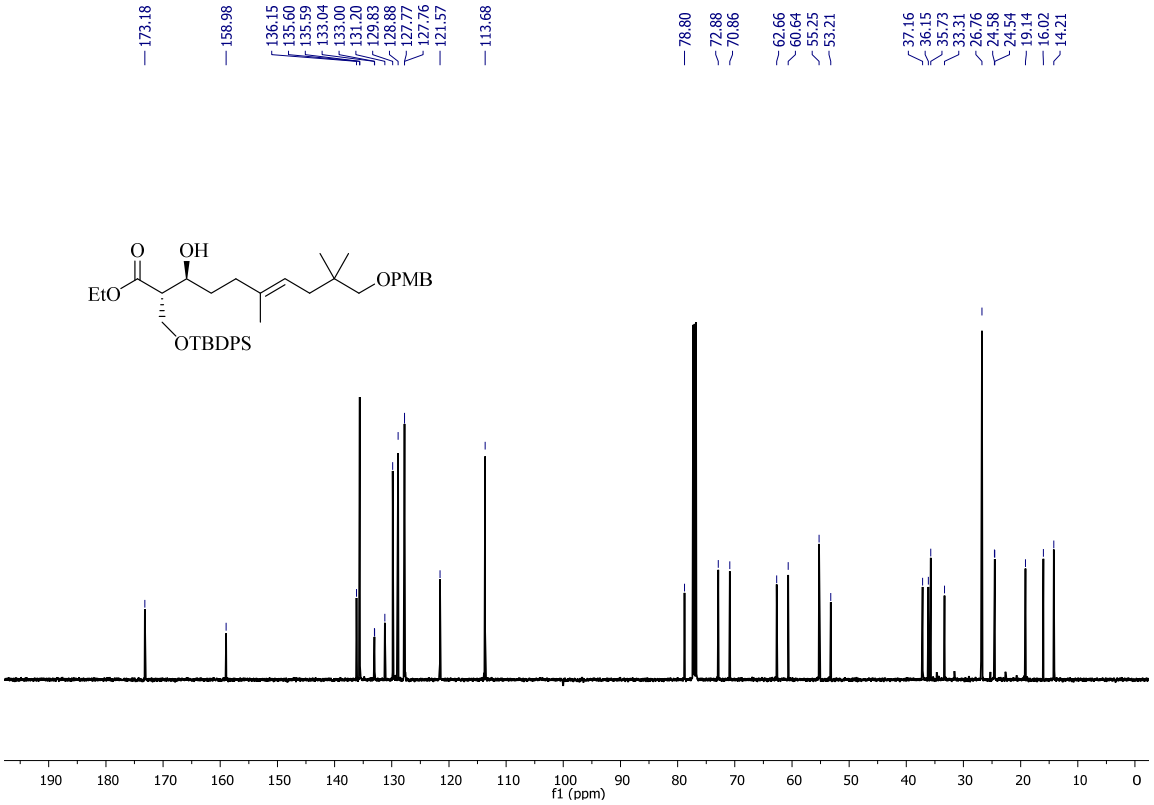
DEPT-135 of compound 47a (125 MHz, $CDCl_3$)



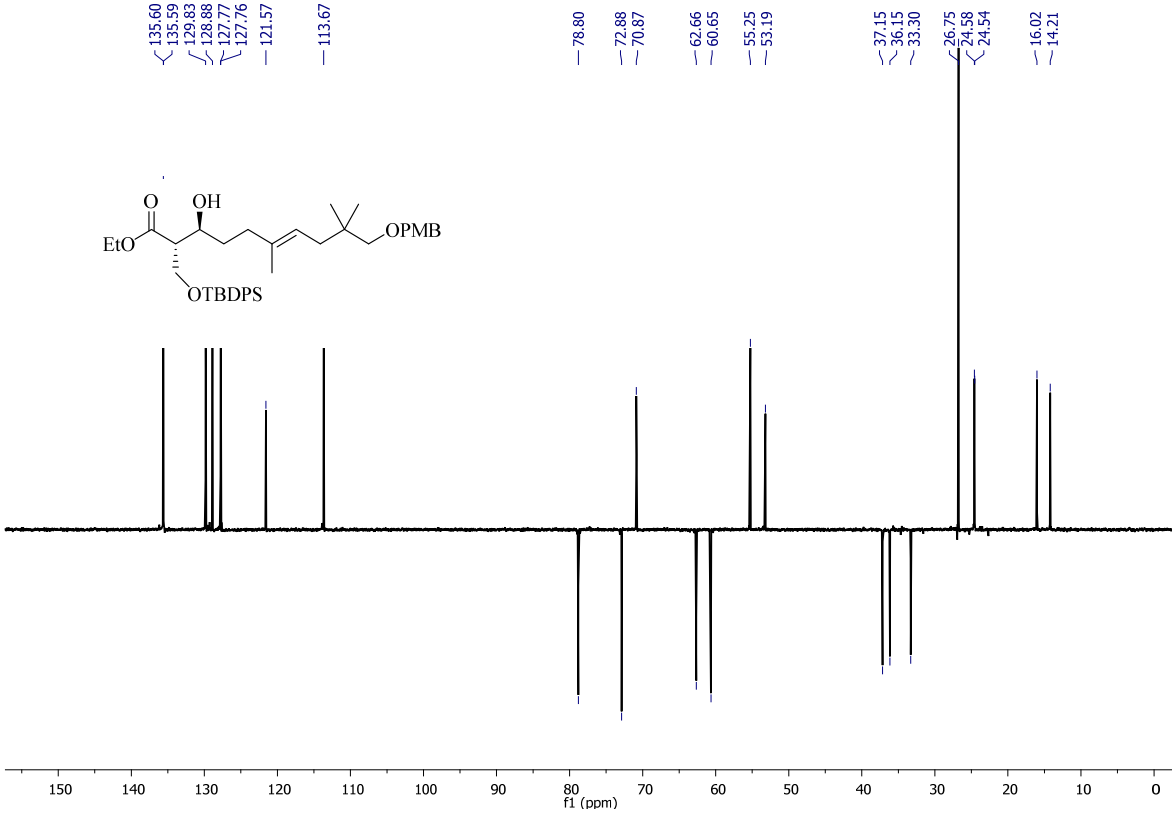
^{1}H NMR of compound 41b (500 MHz, $CDCl_3$)



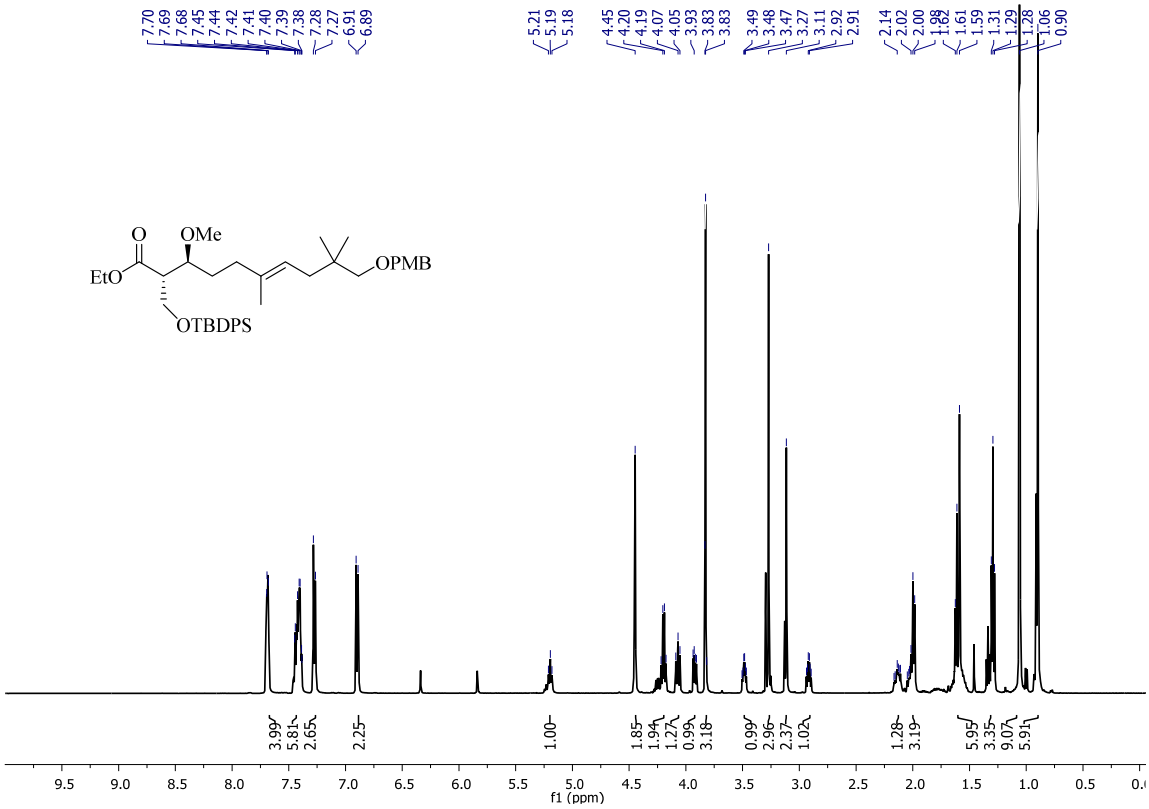
^{13}C NMR of compound 41b (125 MHz, $CDCl_3$)



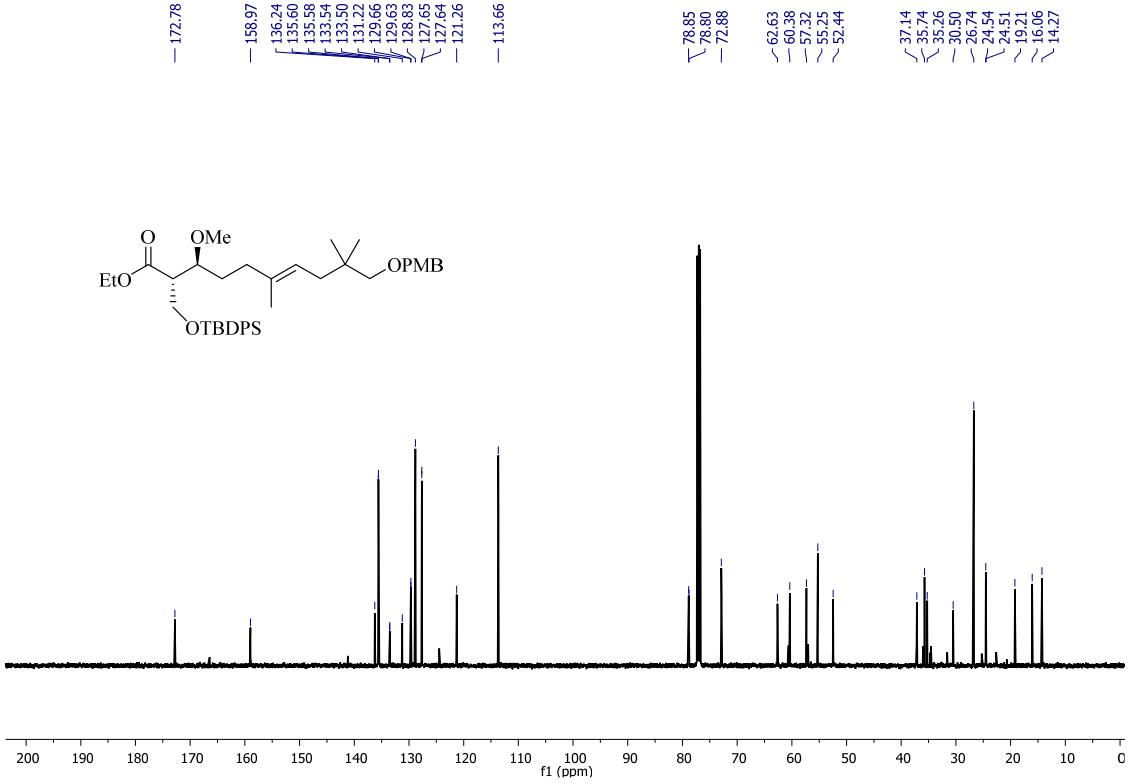
DEPT-135 of compound 41b (125 MHz, $CDCl_3$)



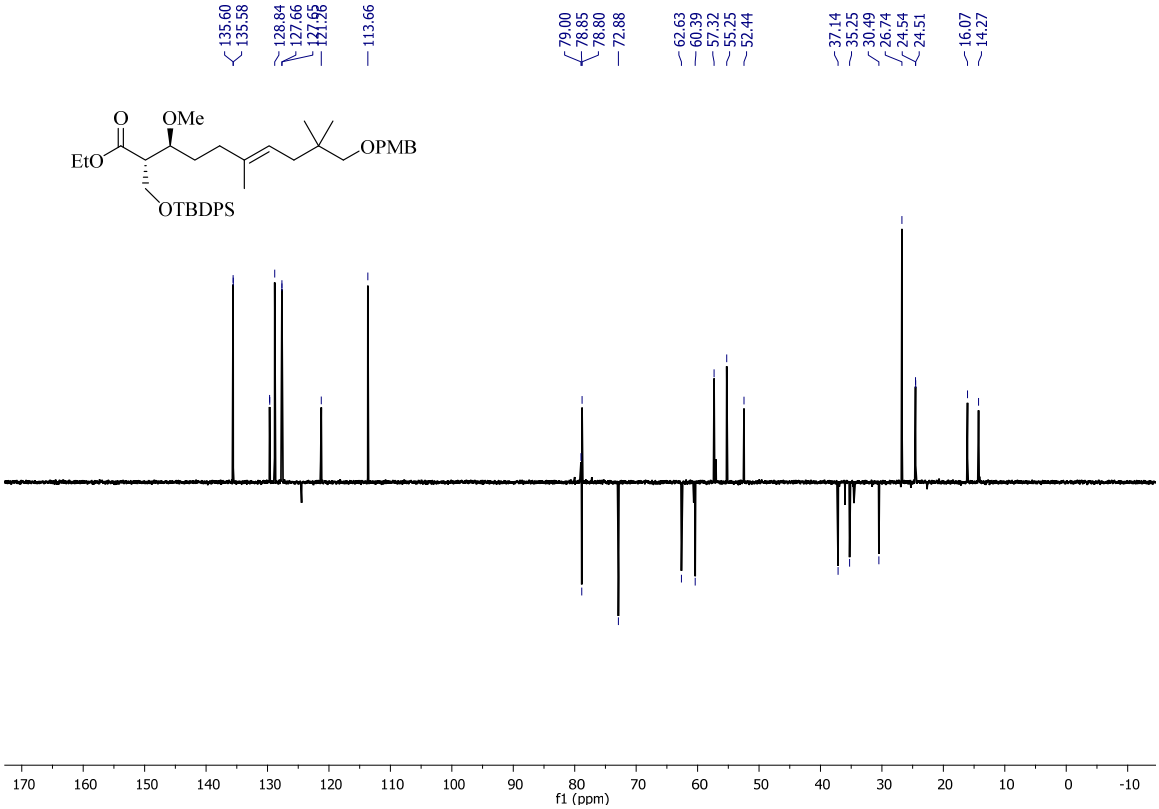
^{1}H NMR of compound 42b (500 MHz, $CDCl_3$)



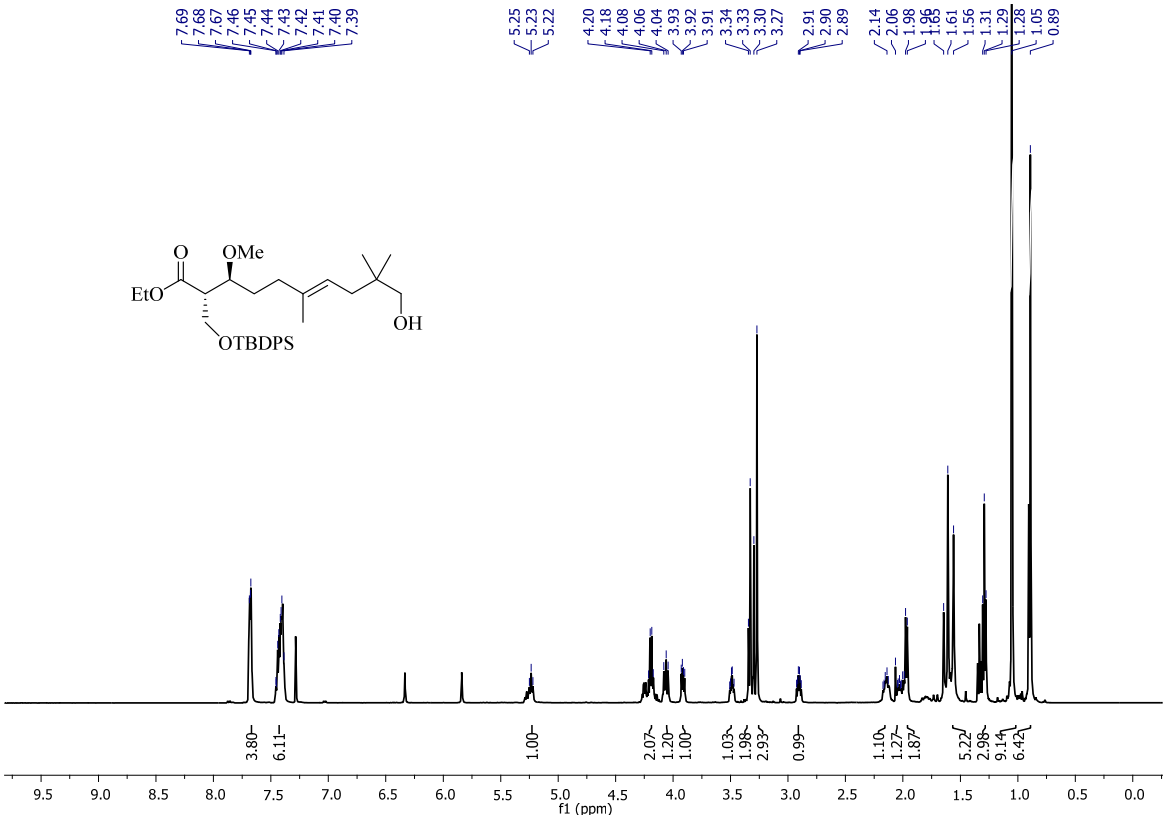
^{13}C NMR of compound 42b (125 MHz, $CDCl_3$)



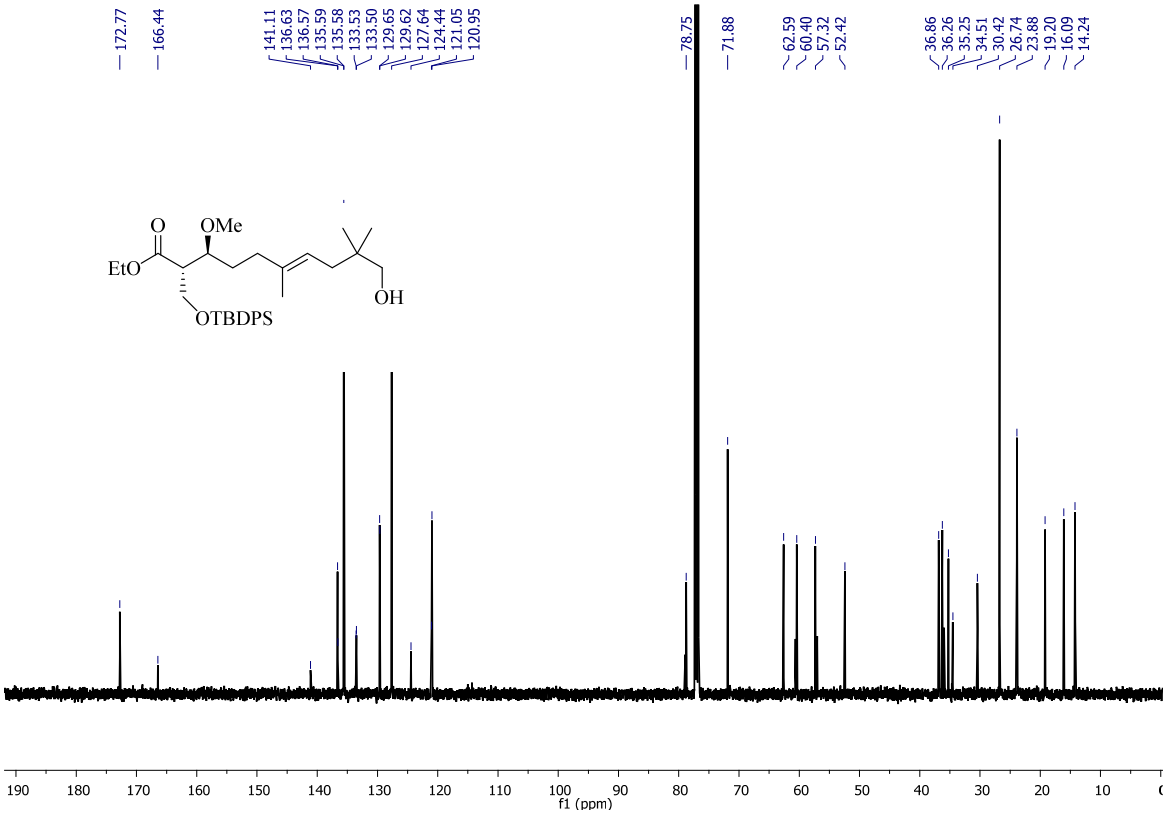
DEPT-135 of compound 42b (125 MHz, $CDCl_3$)



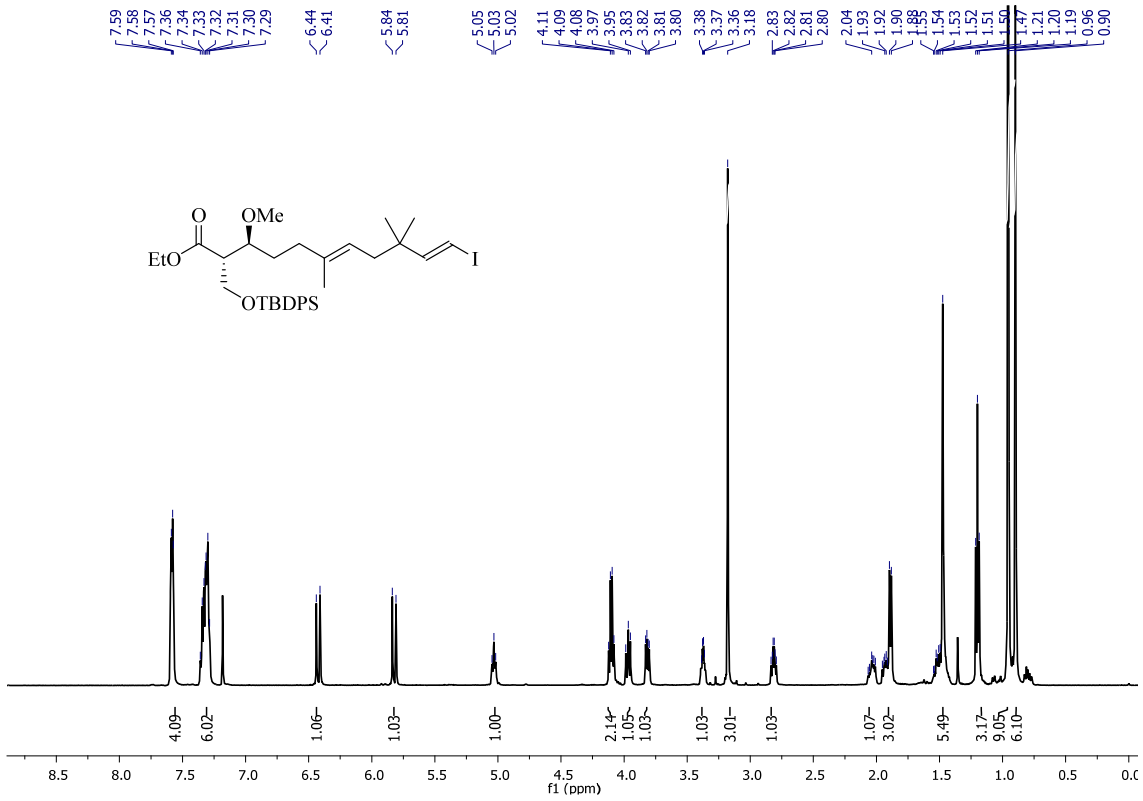
^{1}H NMR of compound 43b (500 MHz, $CDCl_3$)



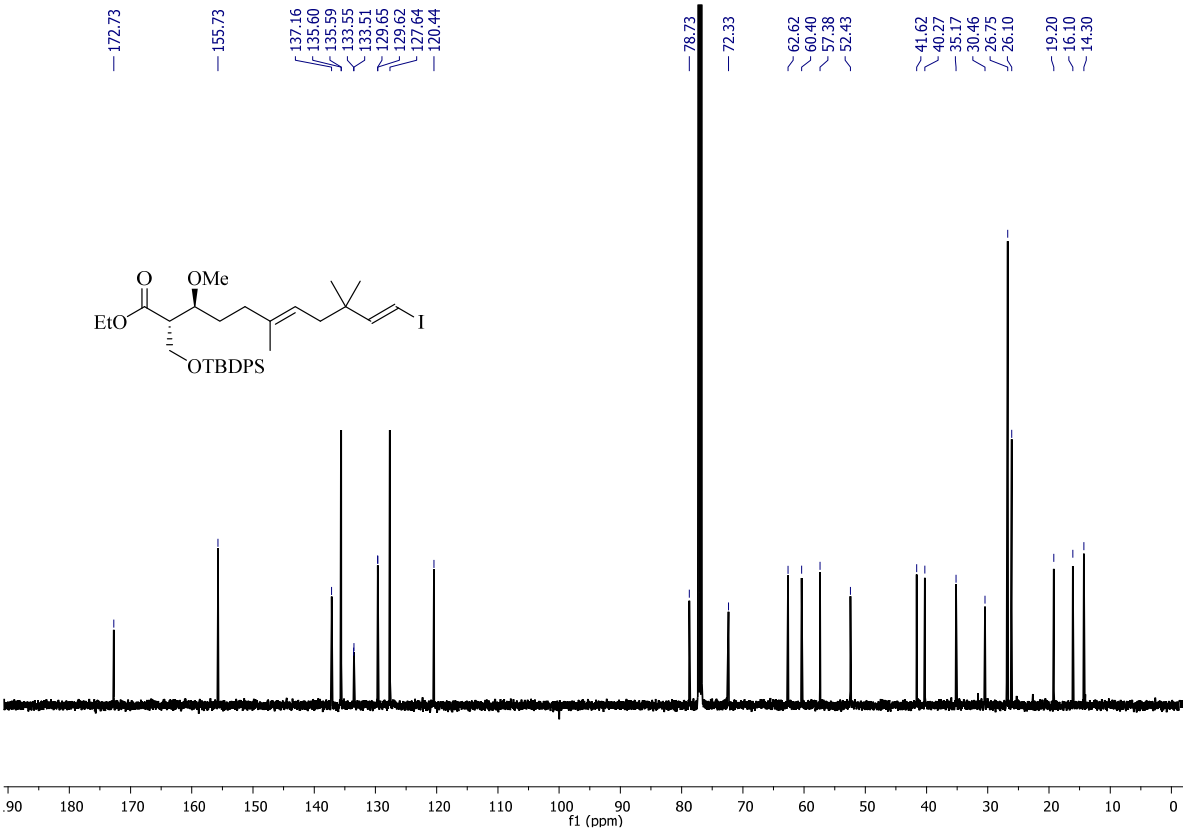
^{13}C NMR of compound 43b (125 MHz, $CDCl_3$)



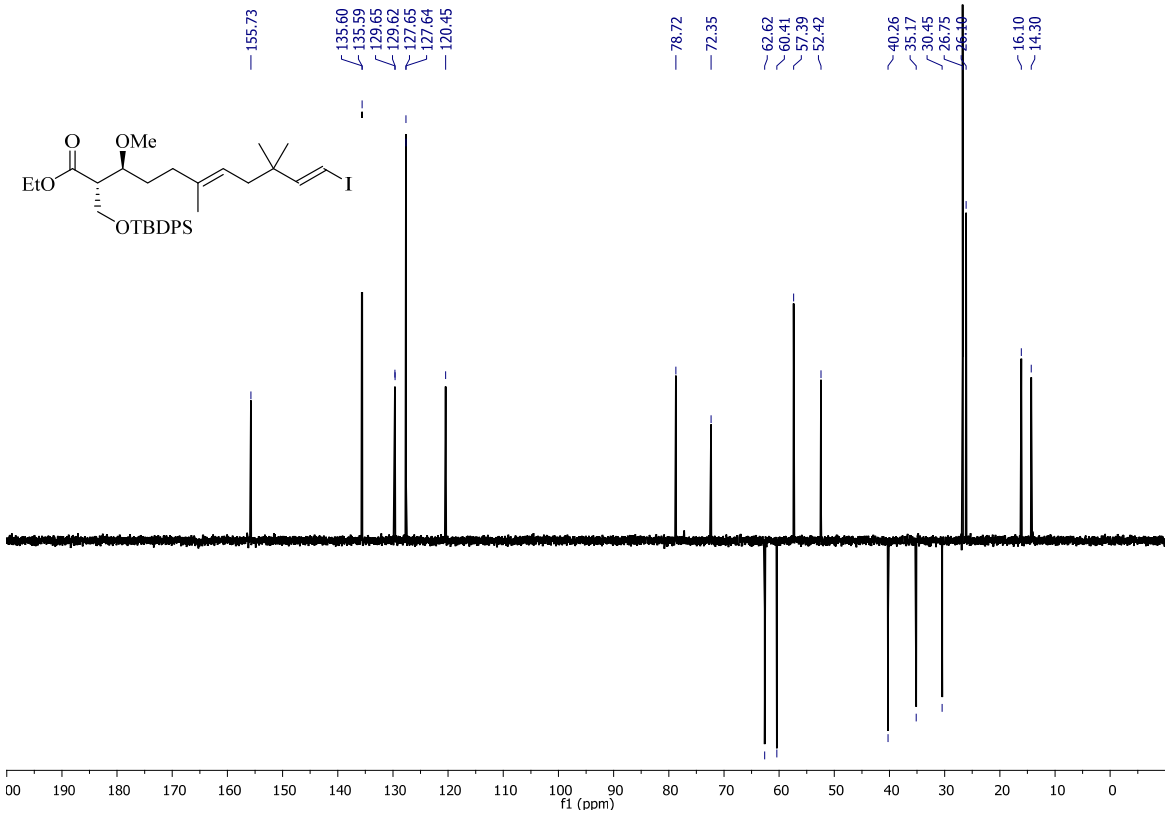
^{1}H NMR of compound 45b (500 MHz, $CDCl_3$)



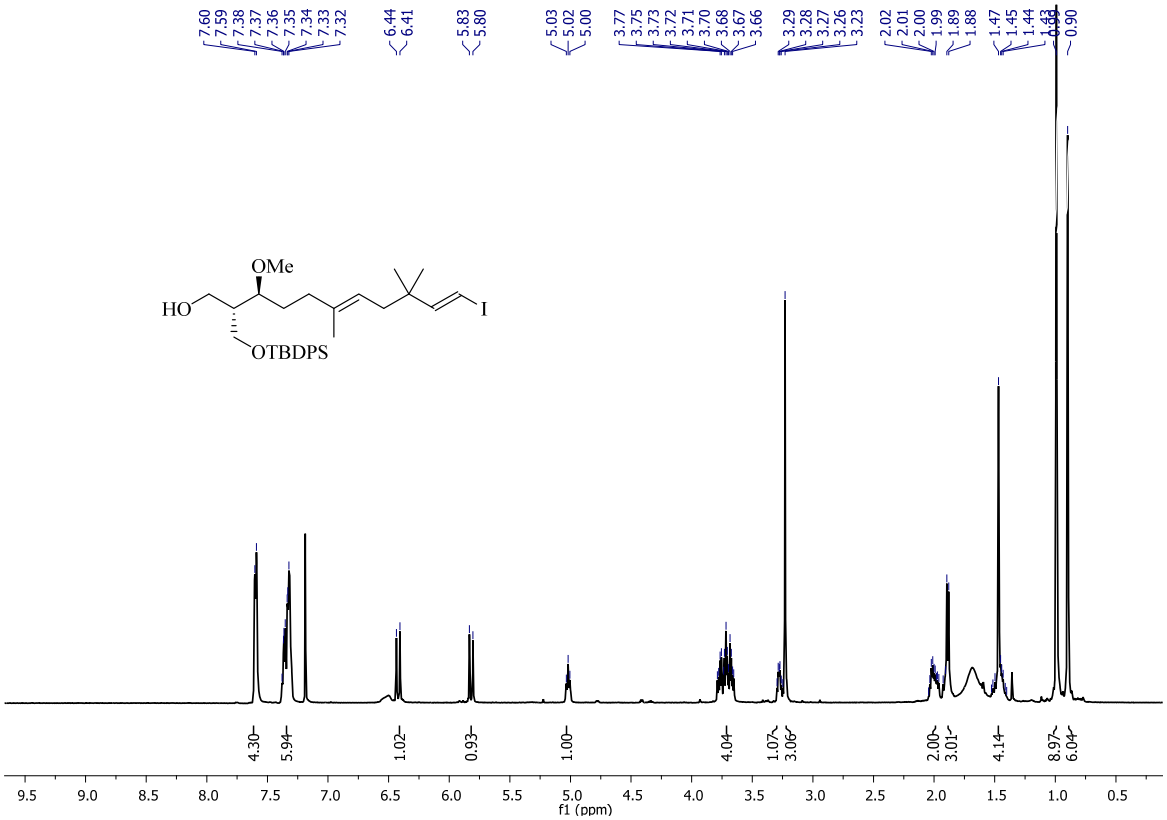
^{13}C NMR of compound 45b (125 MHz, $CDCl_3$)



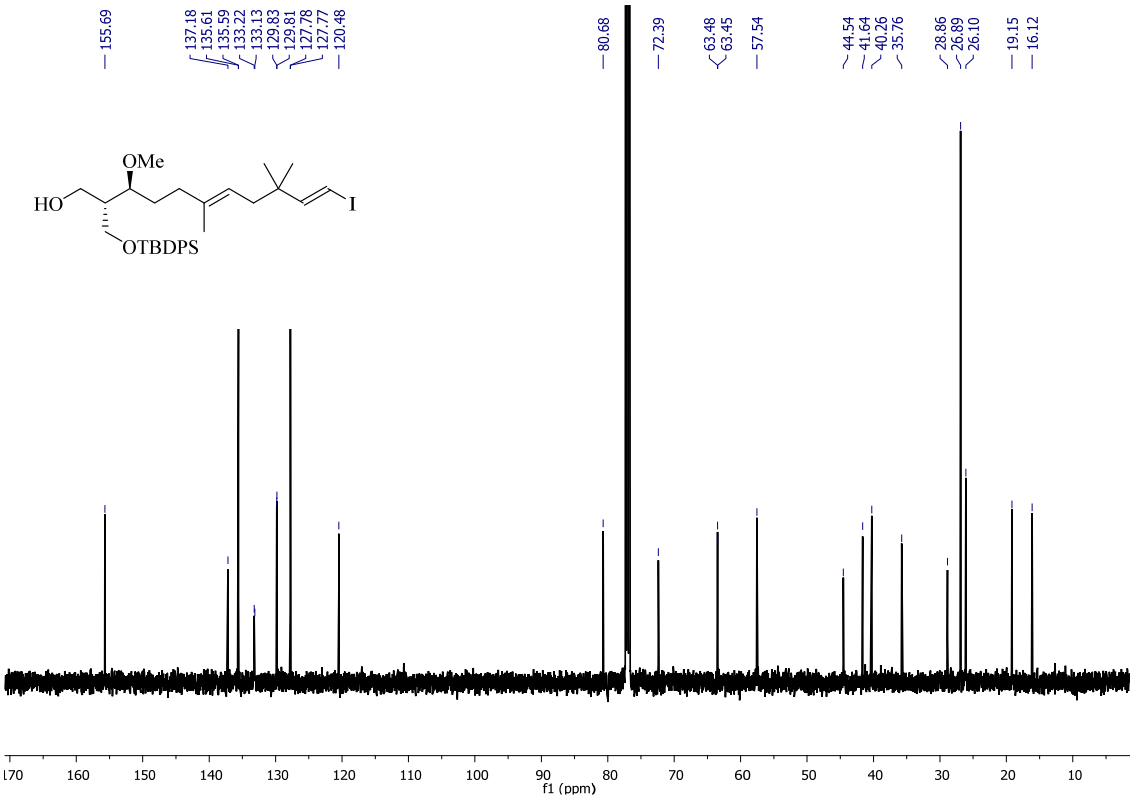
DEPT-135 of compound 45b (125 MHz, $CDCl_3$)



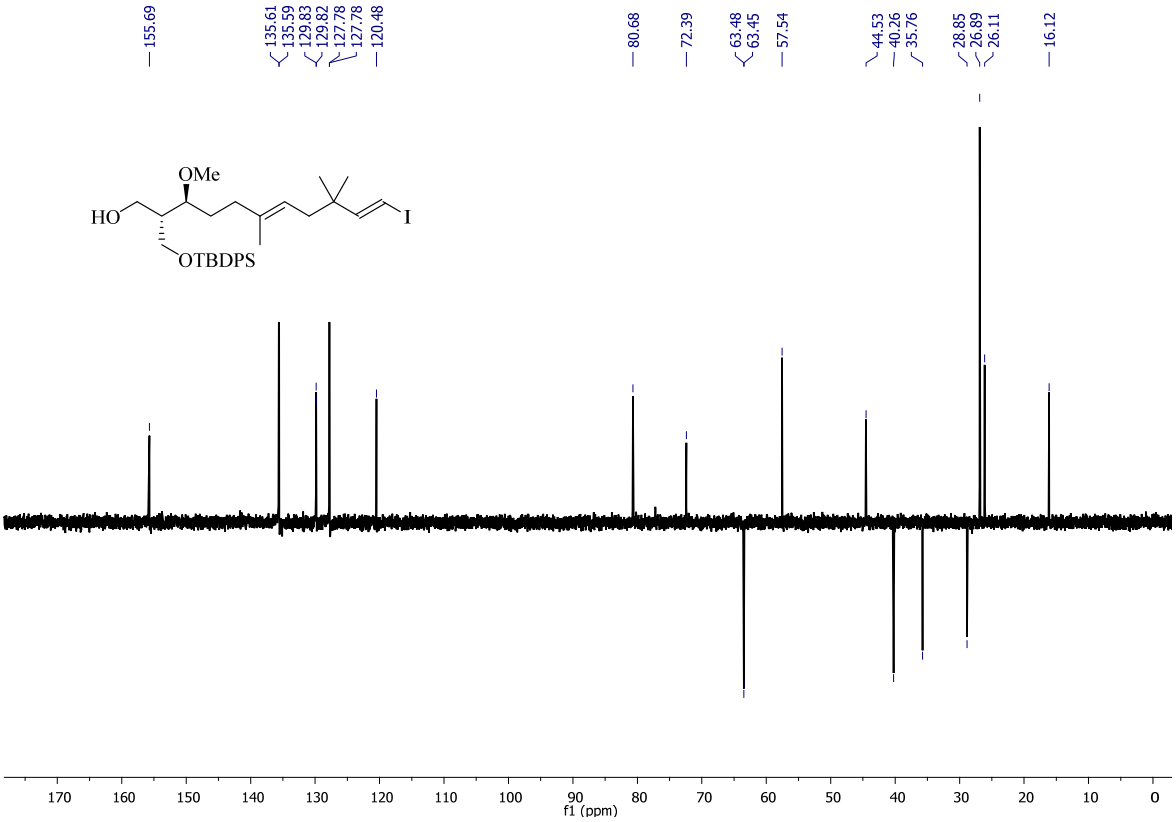
^{1}H NMR of compound 46b (500 MHz, $CDCl_3$)



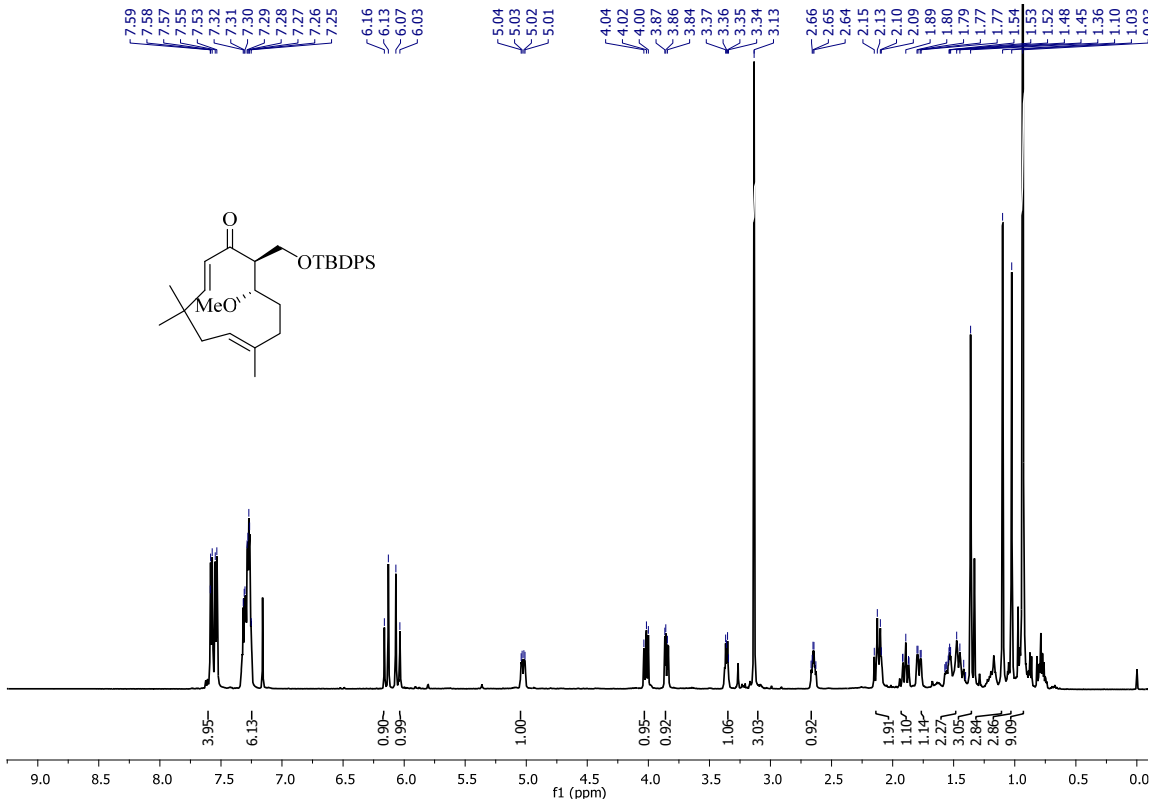
^{13}C NMR of compound 46b (125 MHz, $CDCl_3$)



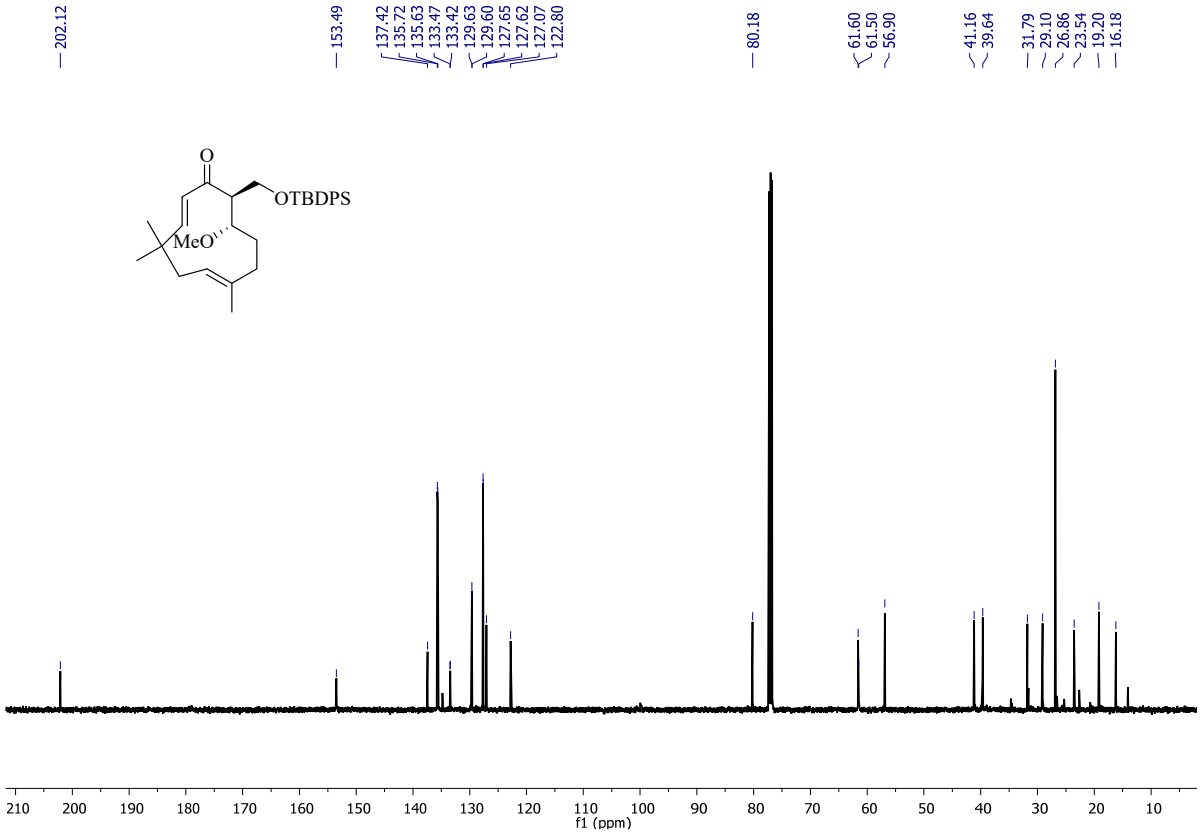
DEPT-135 of compound 46b (125 MHz, $CDCl_3$)



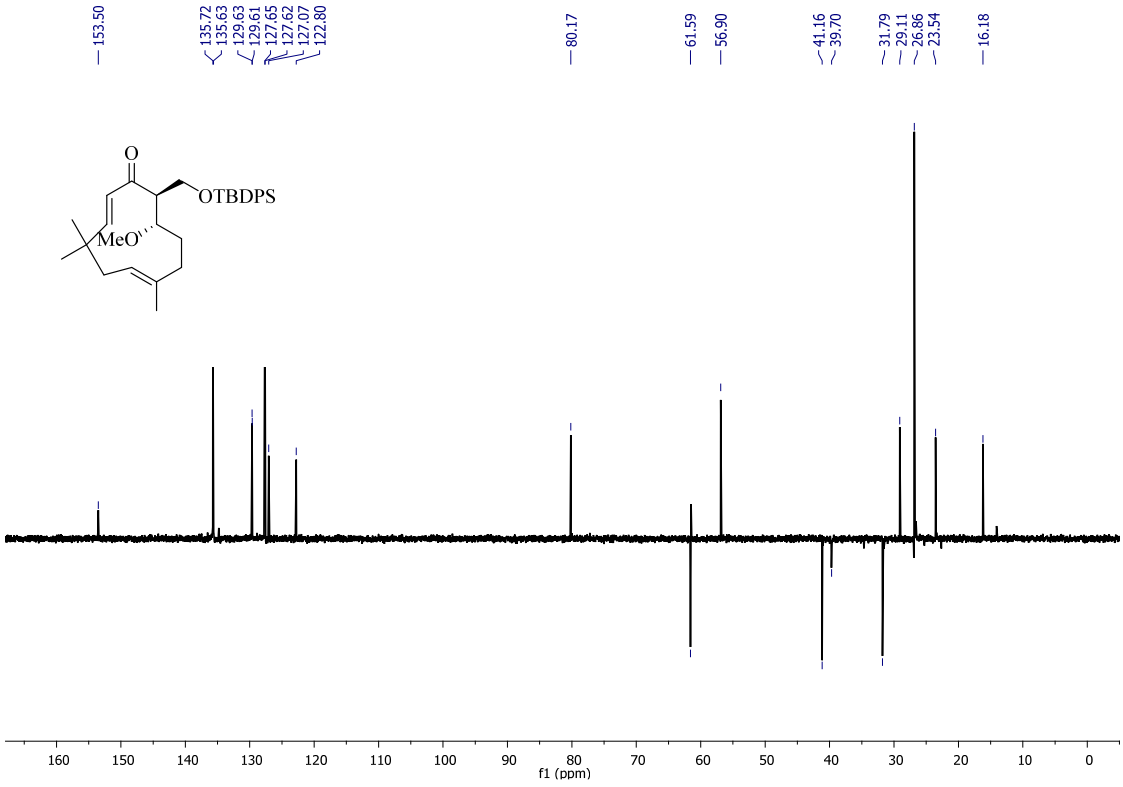
^{1}H NMR of compound 47b (500 MHz, $CDCl_3$)



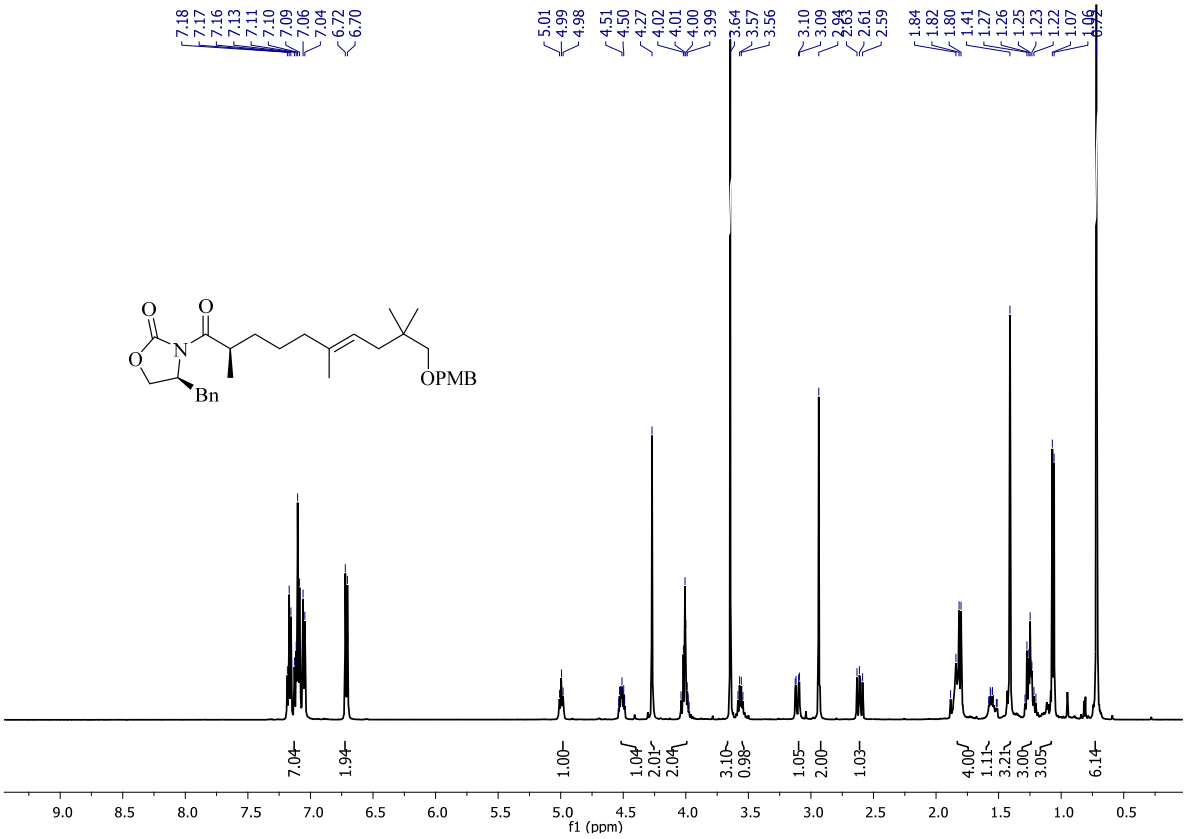
^{13}C NMR of compound 47b (125 MHz, $CDCl_3$)



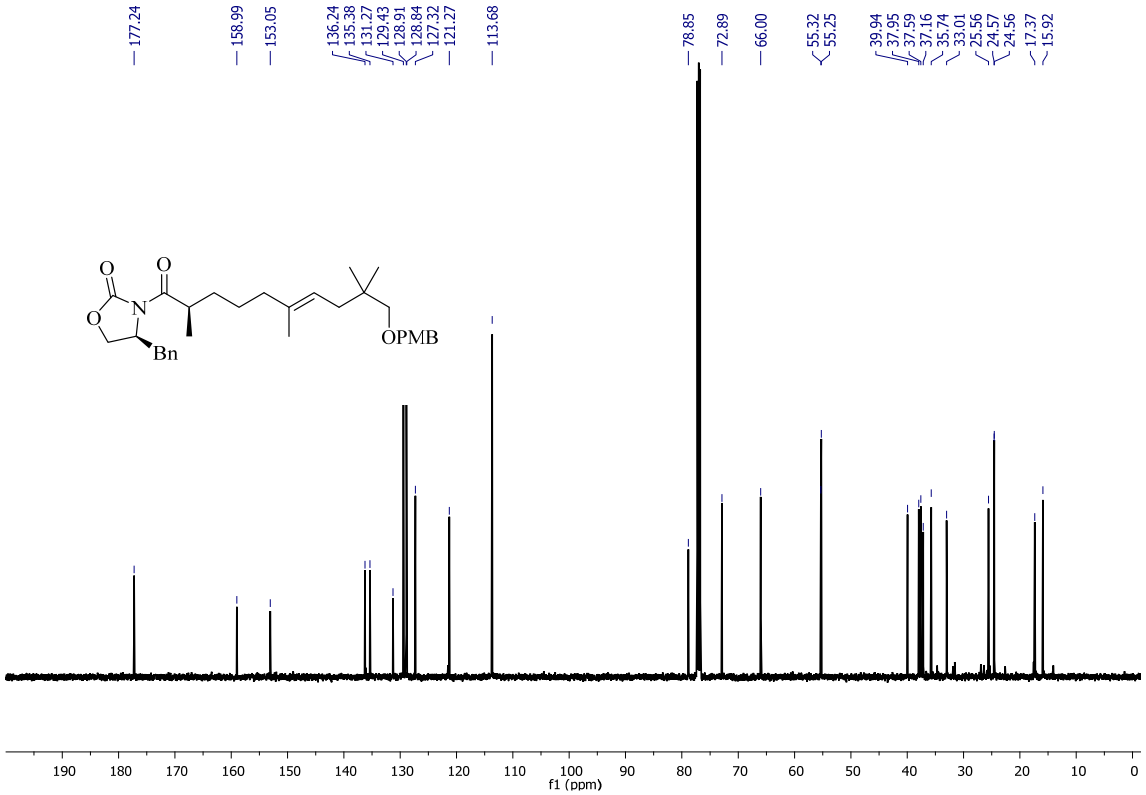
DEPT-135 of compound 47b (125 MHz, $CDCl_3$)



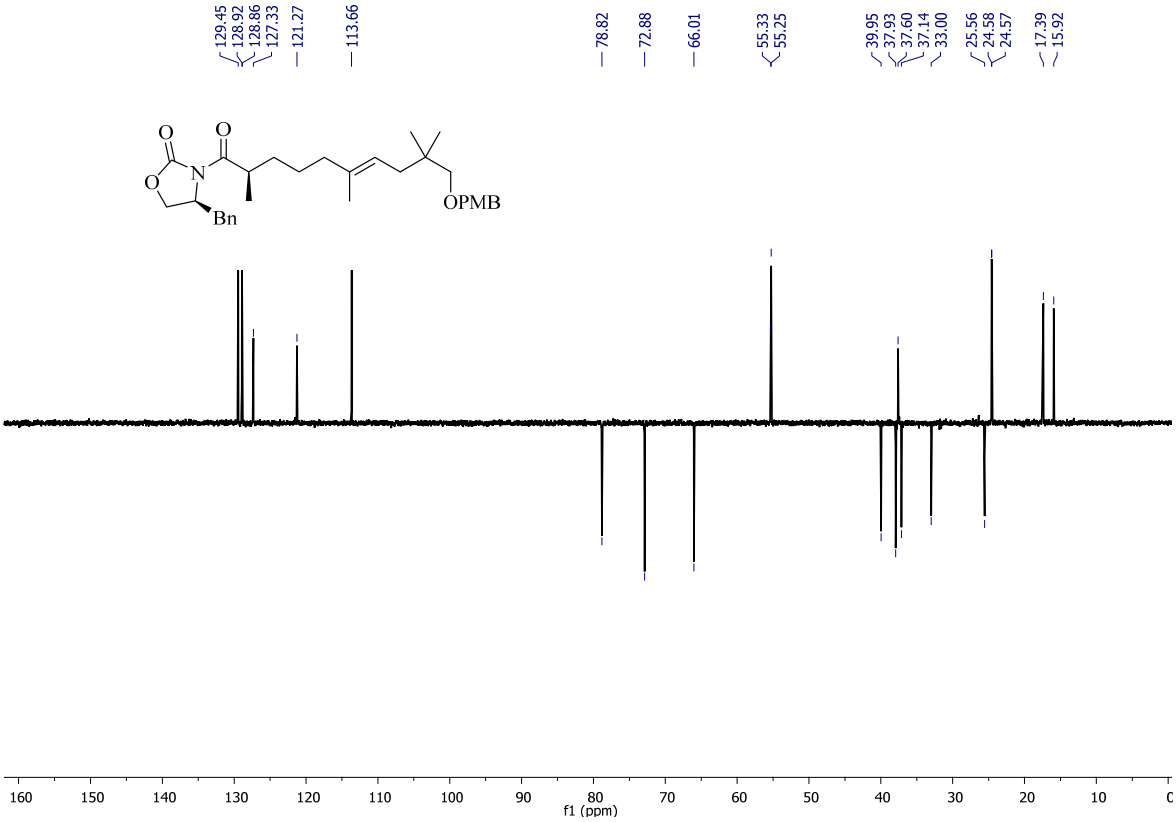
^{1}H NMR of compound 49 (500 MHz, $CDCl_3$)



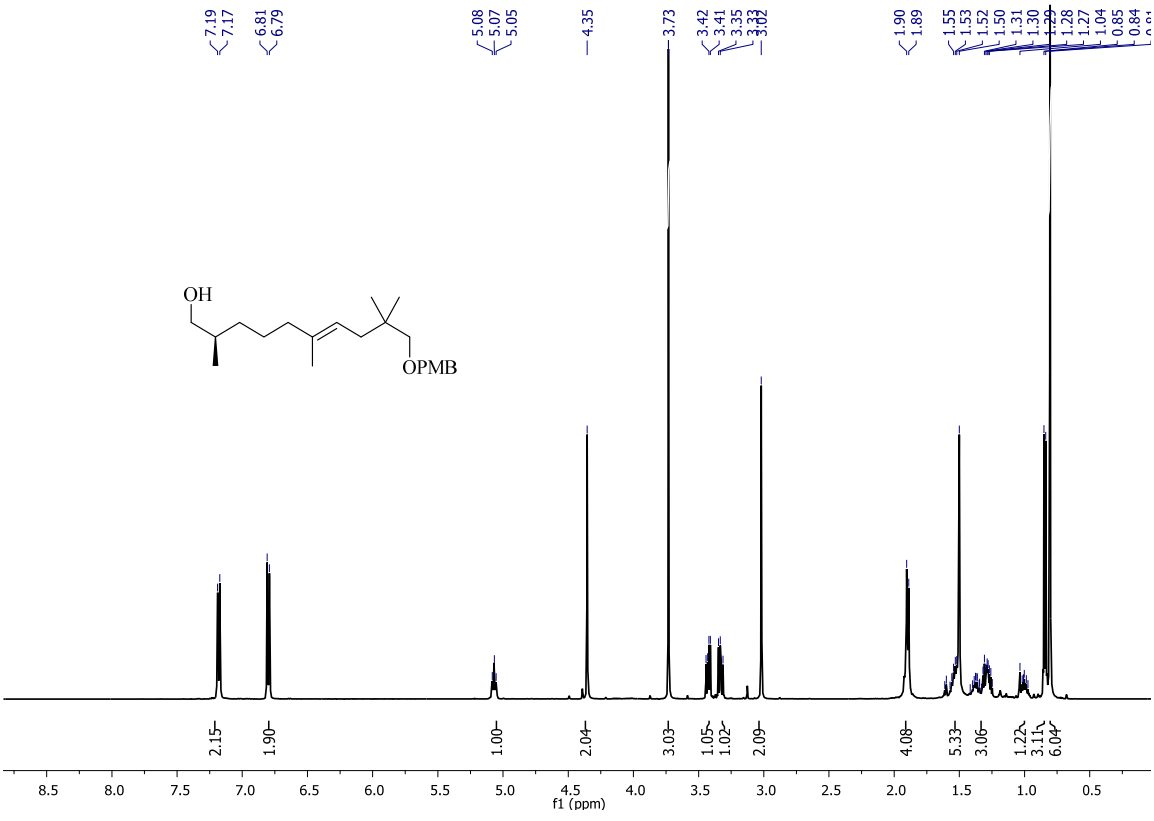
^{13}C NMR of compound 49 (125 MHz, $CDCl_3$)



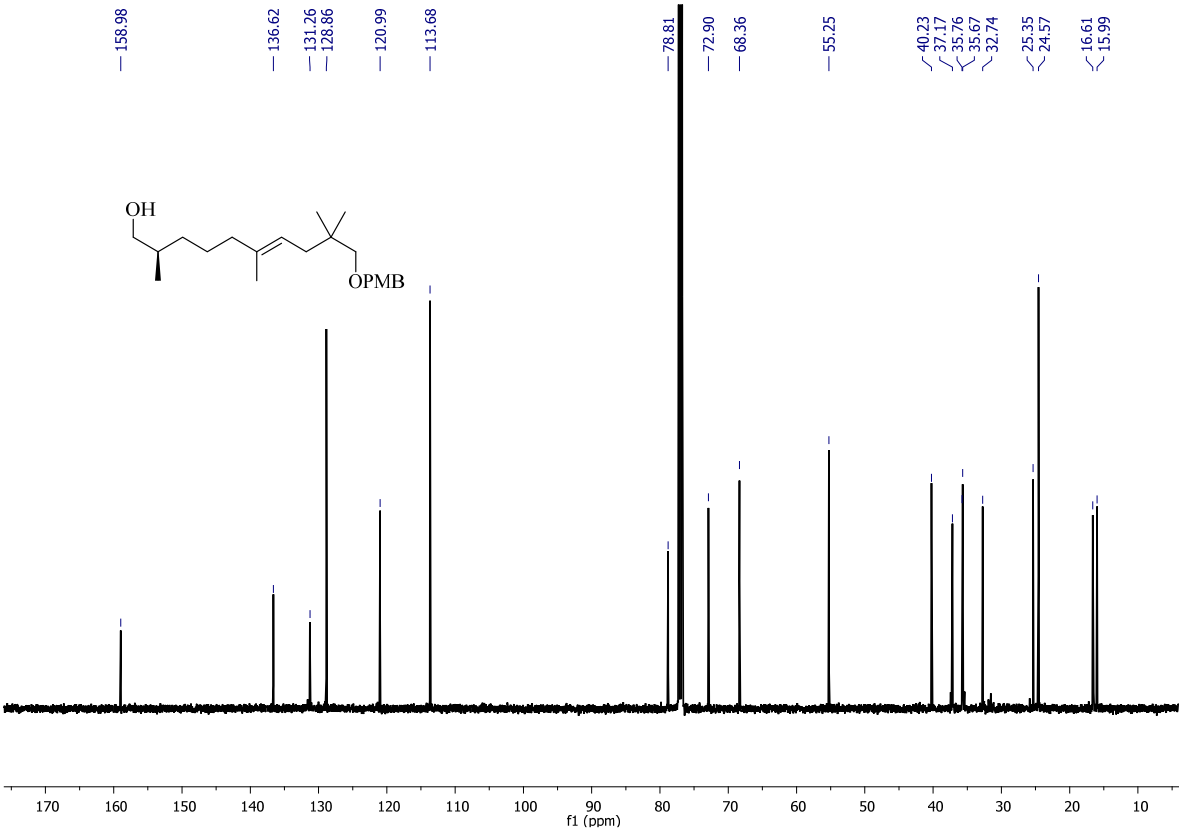
DEPT-135 of compound 49 (125 MHz, $CDCl_3$)



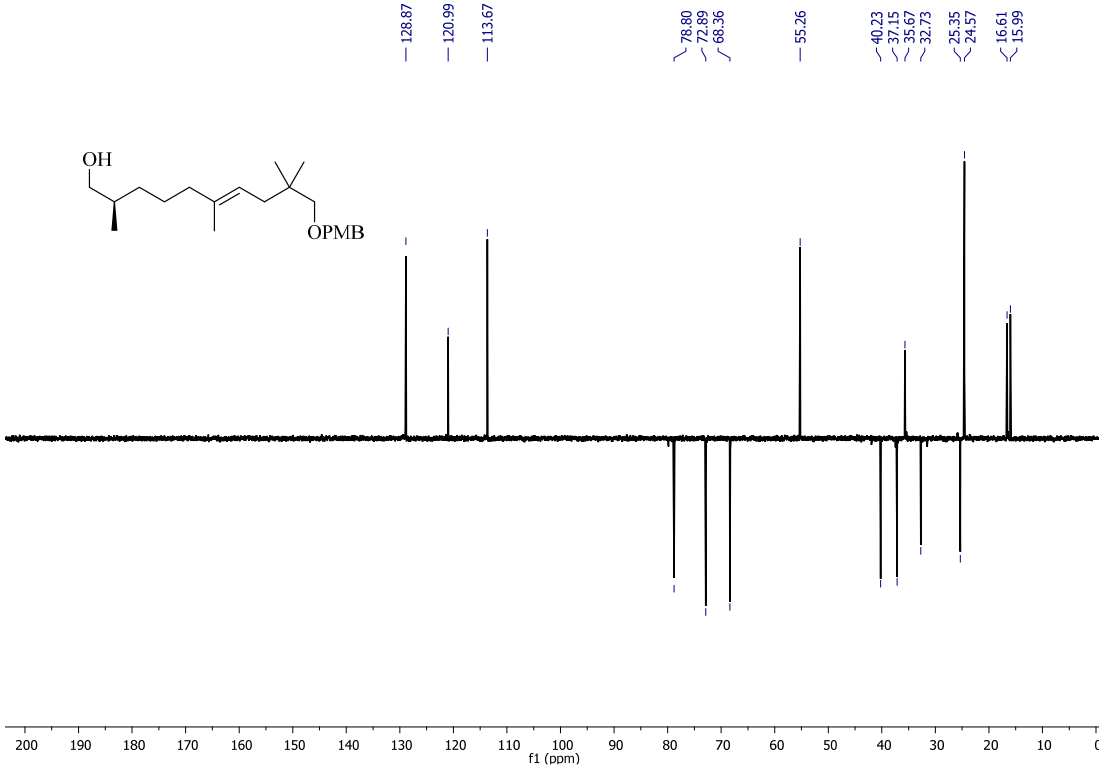
^{1}H NMR of compound 50 (500 MHz, $CDCl_3$)



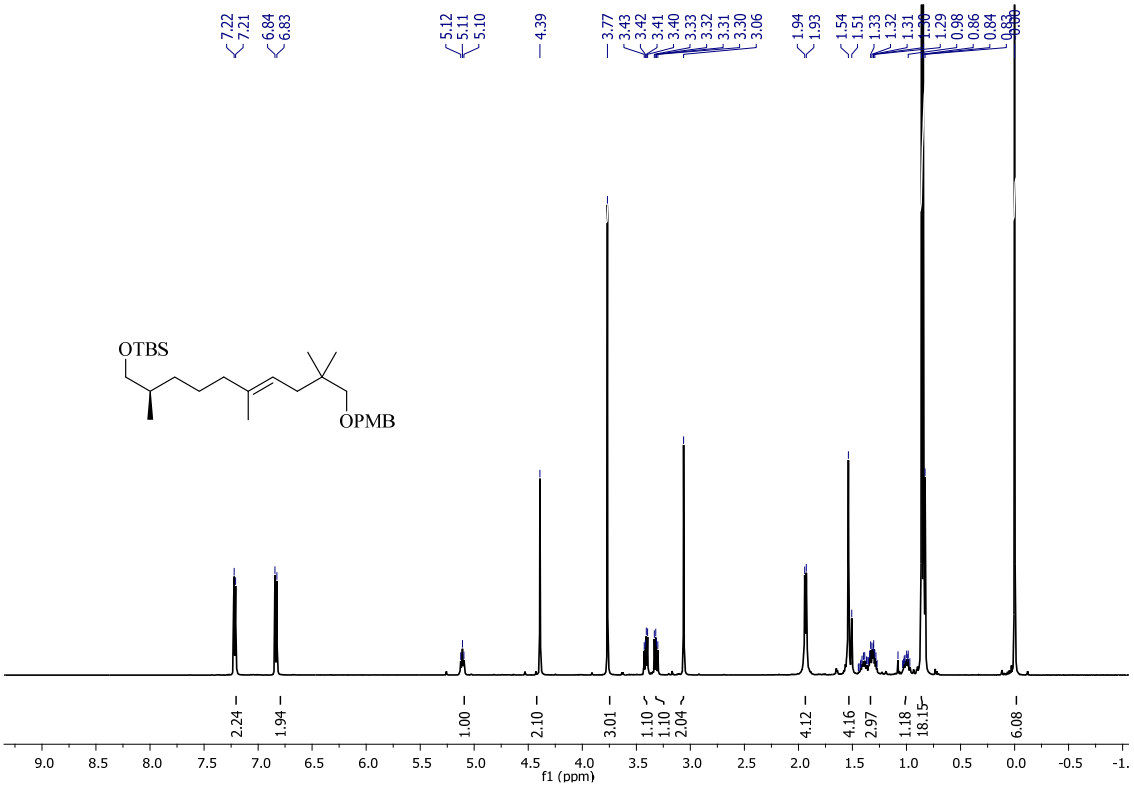
^{13}C NMR of compound 50 (125 MHz, $CDCl_3$)



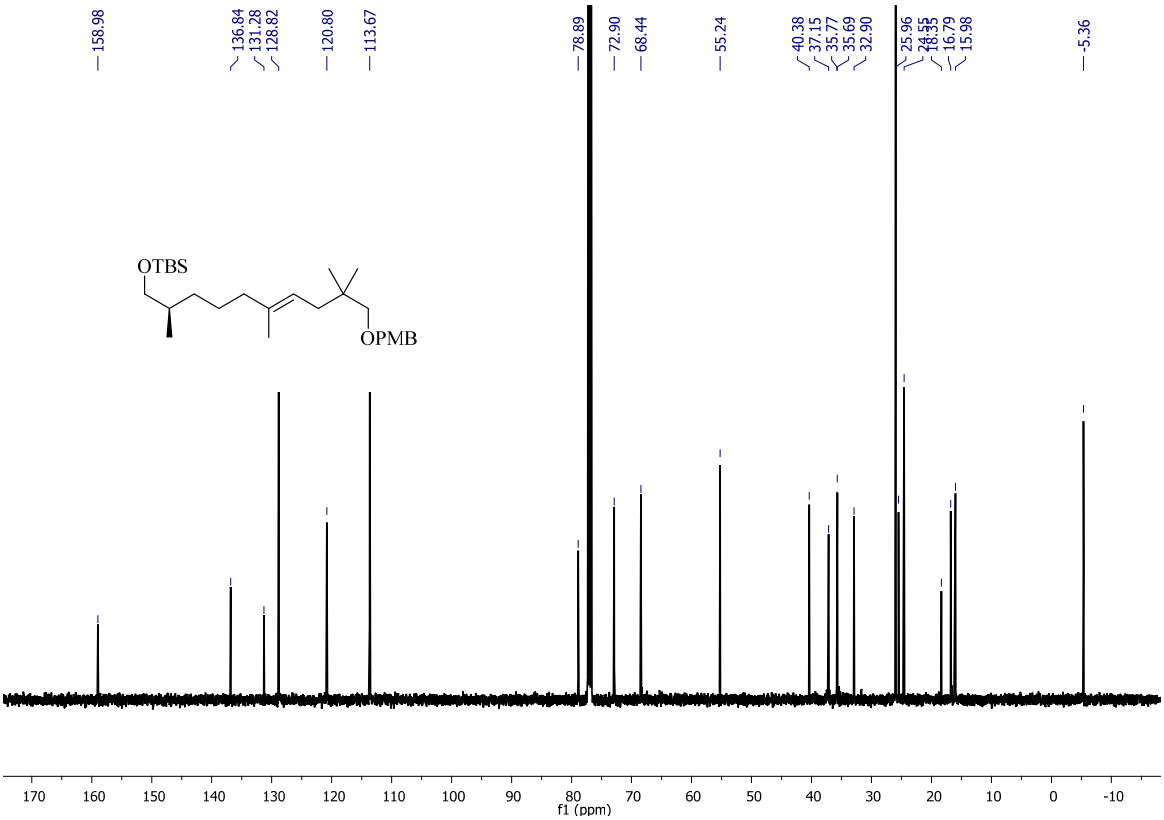
DEPT-135 of compound 50 (125 MHz, $CDCl_3$)



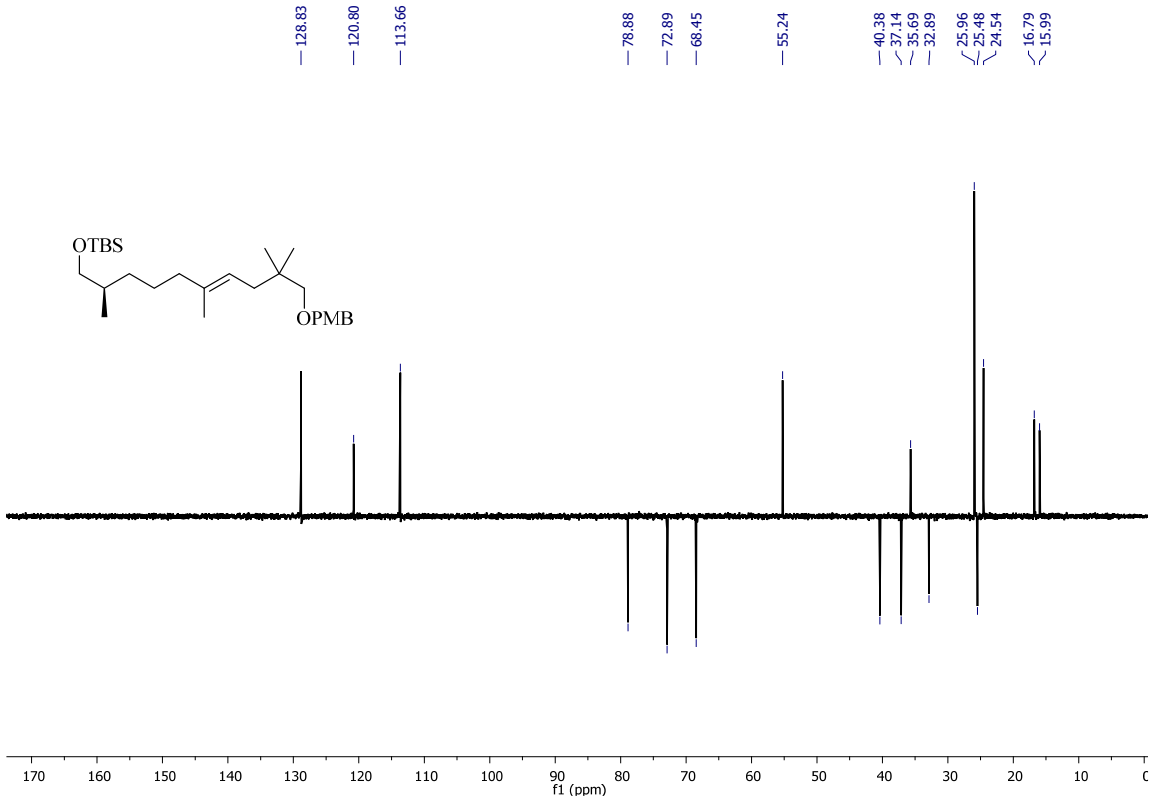
^{1}H NMR of compound 51 (500 MHz, $CDCl_3$)



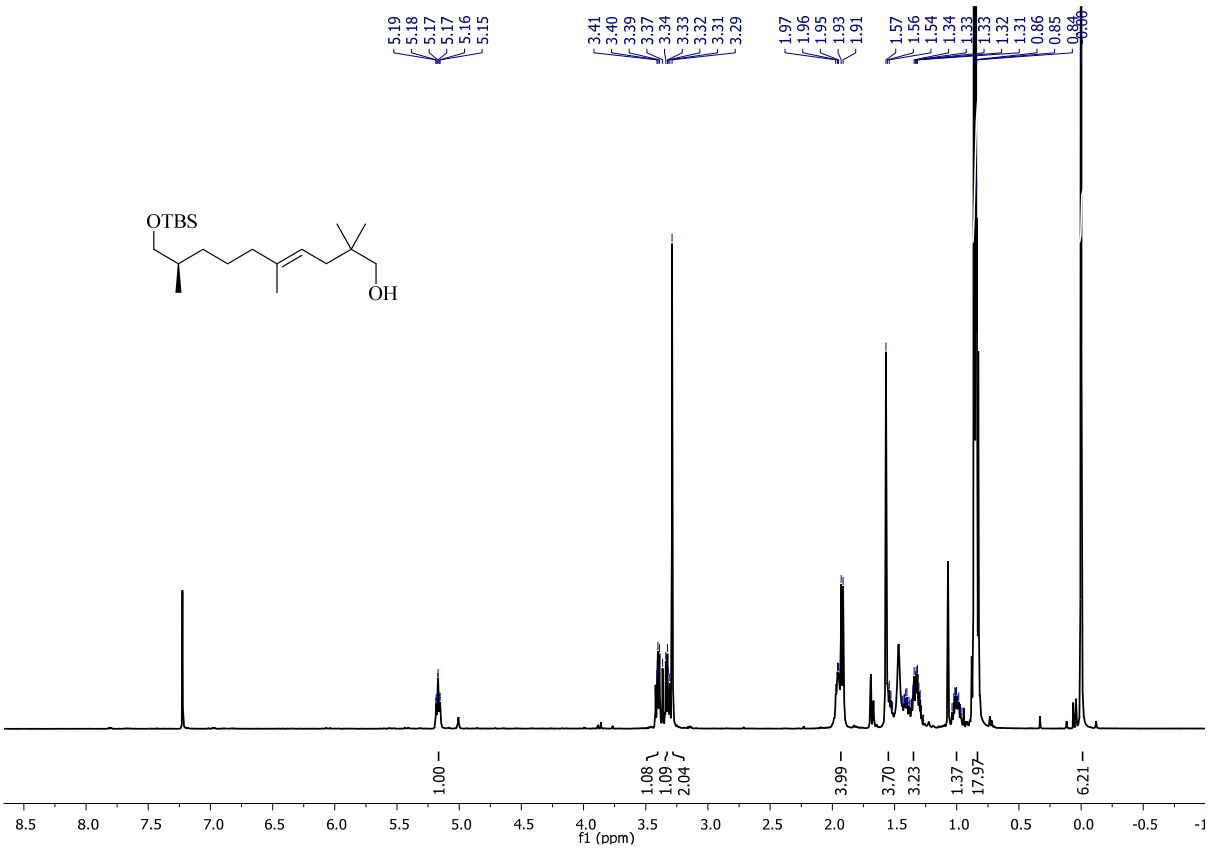
^{13}C NMR of compound 51 (125 MHz, $CDCl_3$)



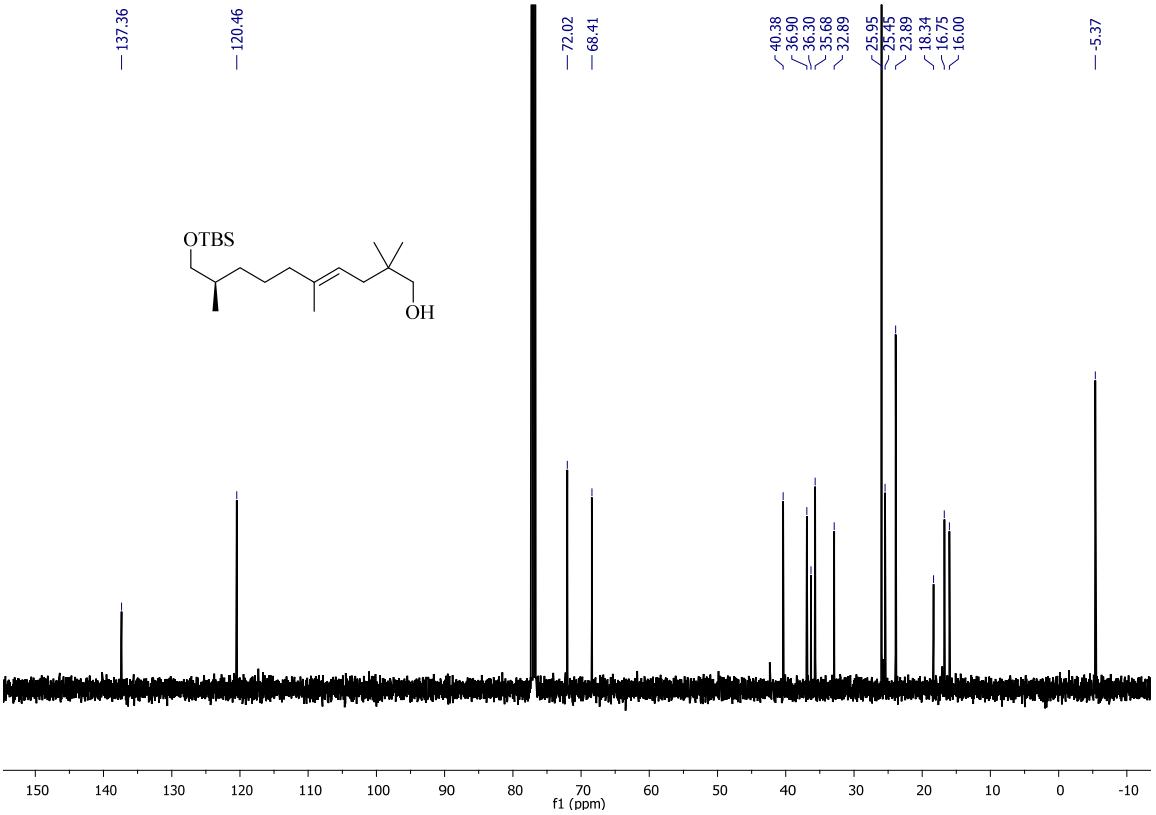
DEPT-135 of compound 51 (125 MHz, $CDCl_3$)



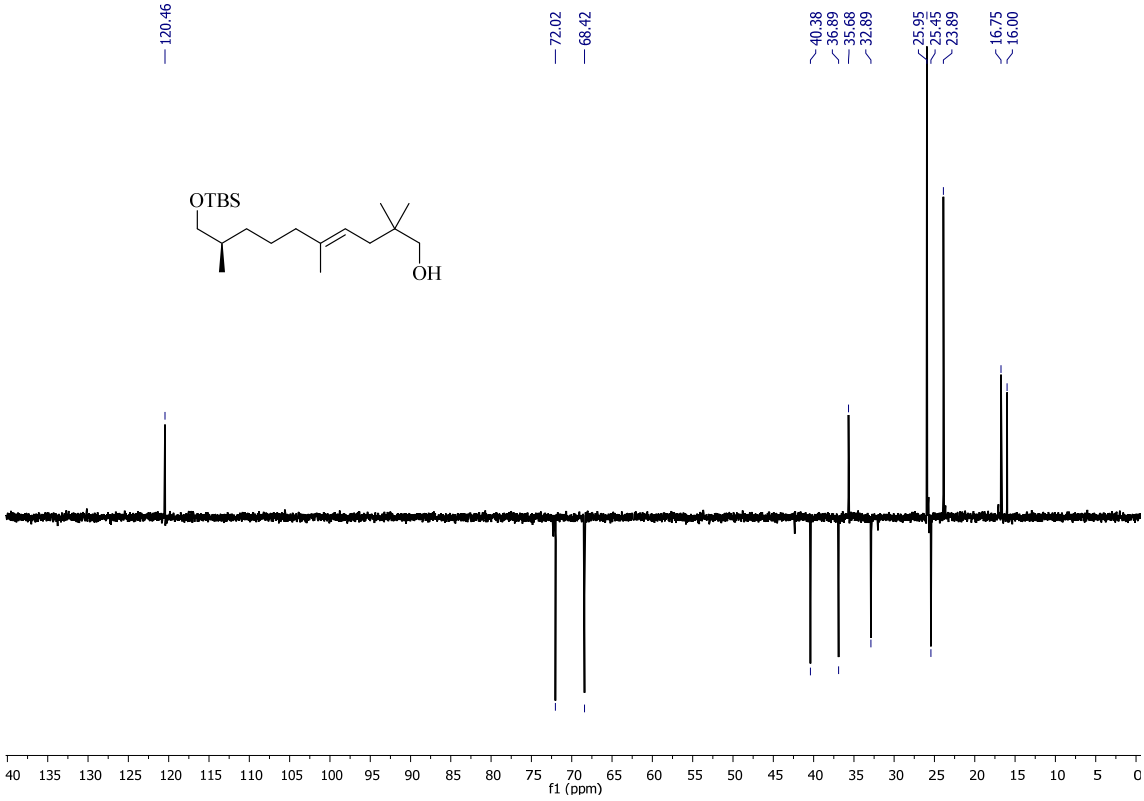
^{1}H NMR of compound 52 (500 MHz, $CDCl_3$)



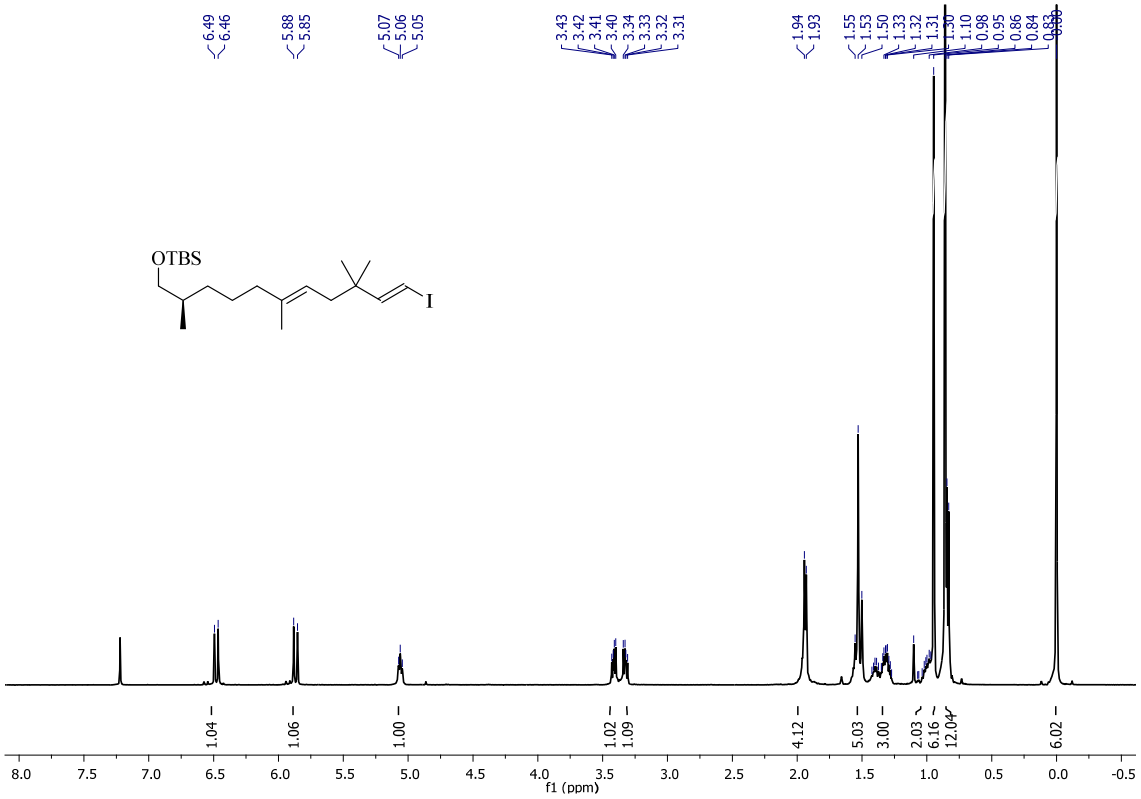
^{13}C NMR of compound 52 (125 MHz, $CDCl_3$)



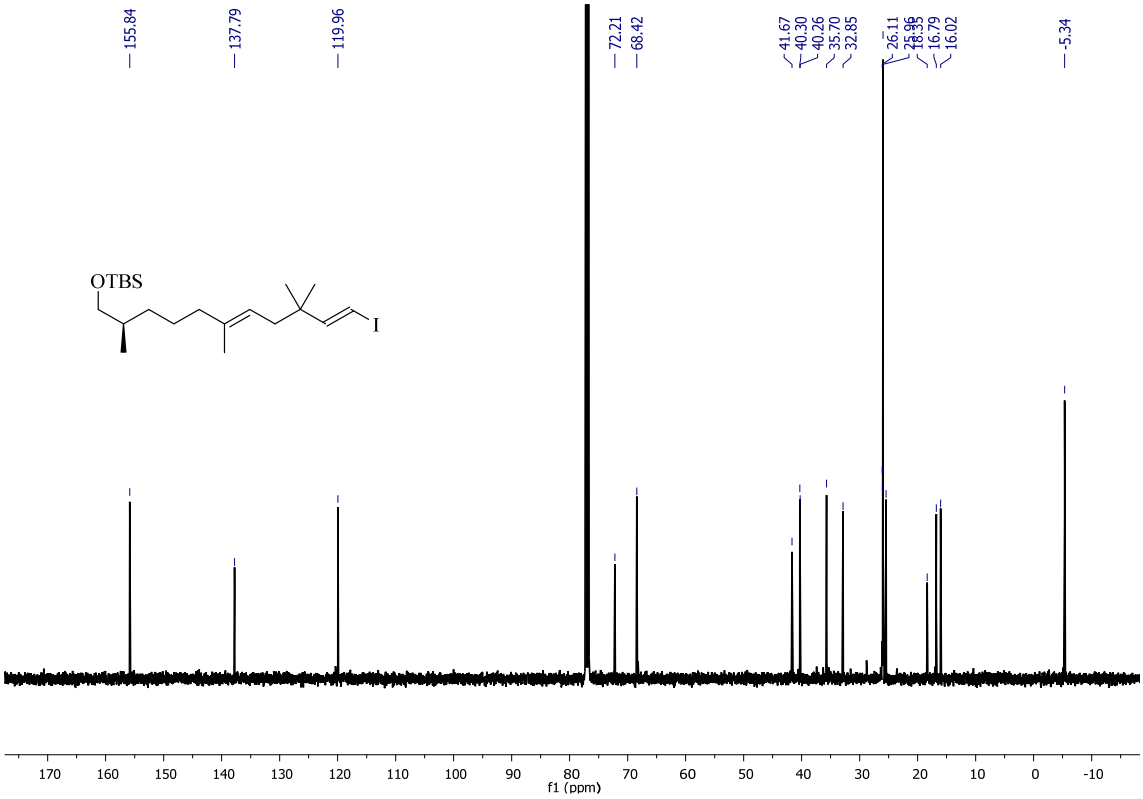
DEPT-135 of compound 52 (125 MHz, $CDCl_3$)



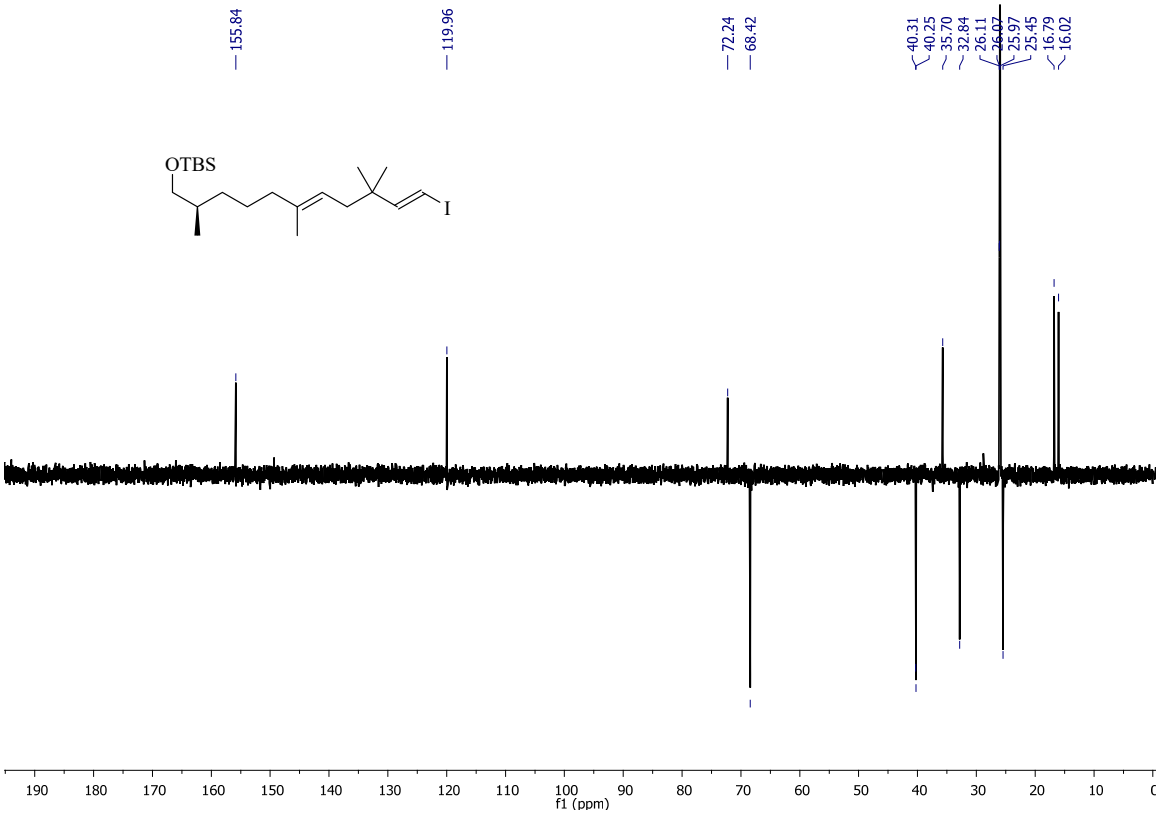
^{1}H NMR of compound 54 (500 MHz, $CDCl_3$)



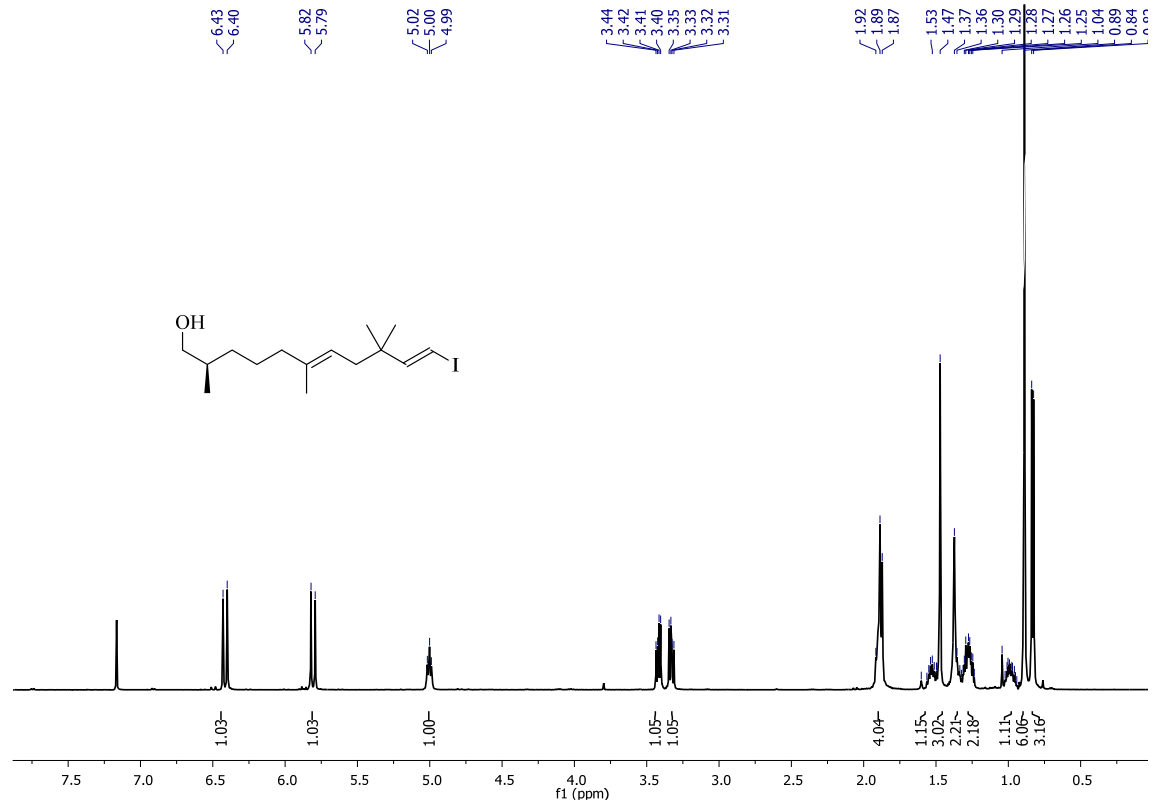
^{13}C NMR of compound 54 (125 MHz, $CDCl_3$)



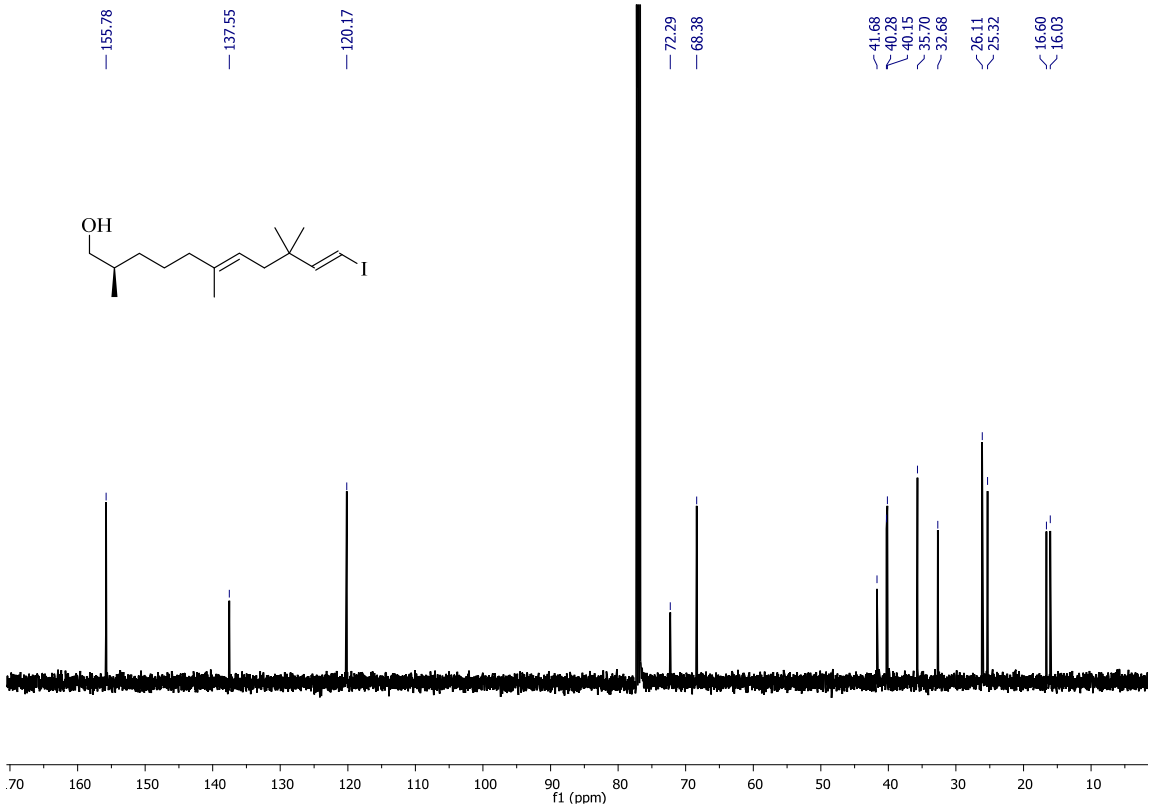
DEPT-135 of compound 54 (125 MHz, $CDCl_3$)



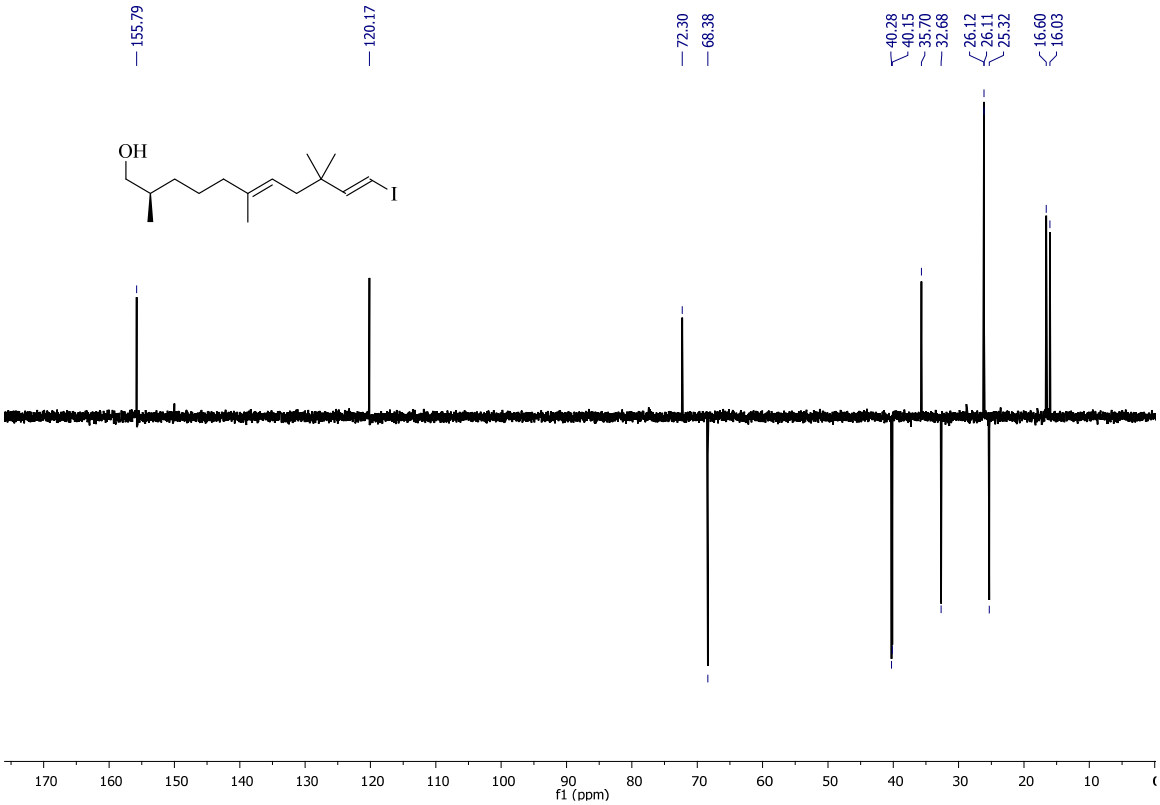
^{1}H NMR of compound 55 (500 MHz, $CDCl_3$)



^{13}C NMR of compound 55 (125 MHz, $CDCl_3$)

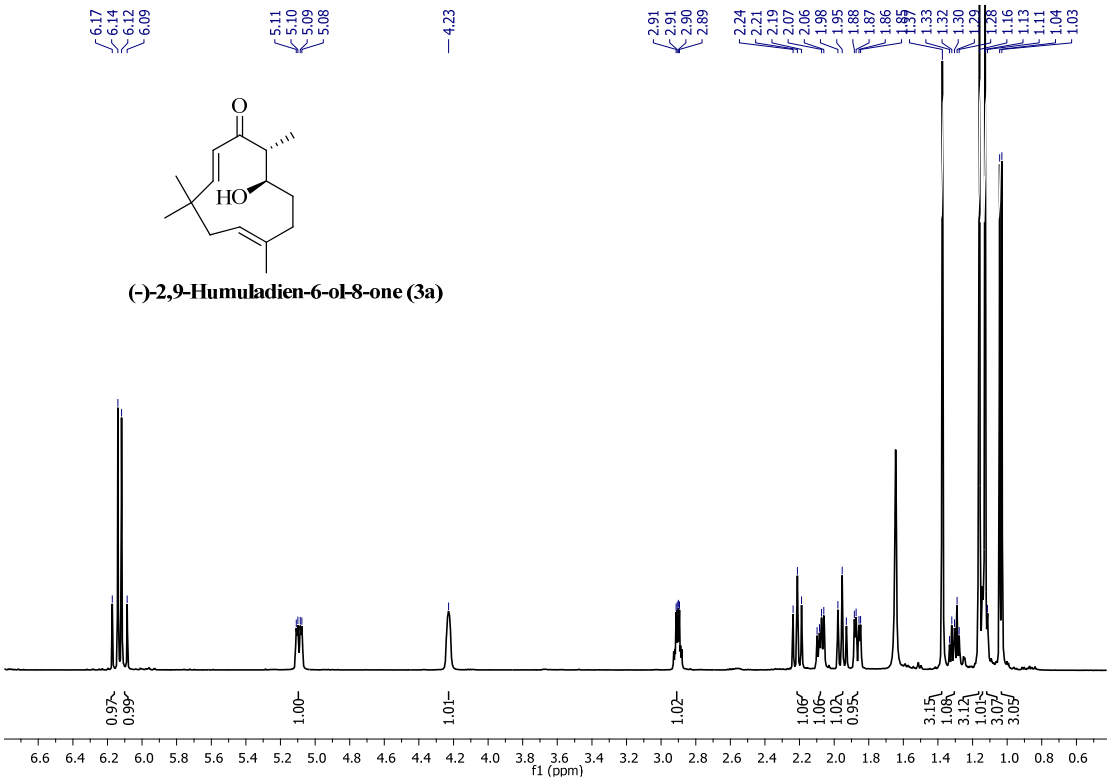


DEPT-135 of compound 55 (125 MHz, $CDCl_3$)

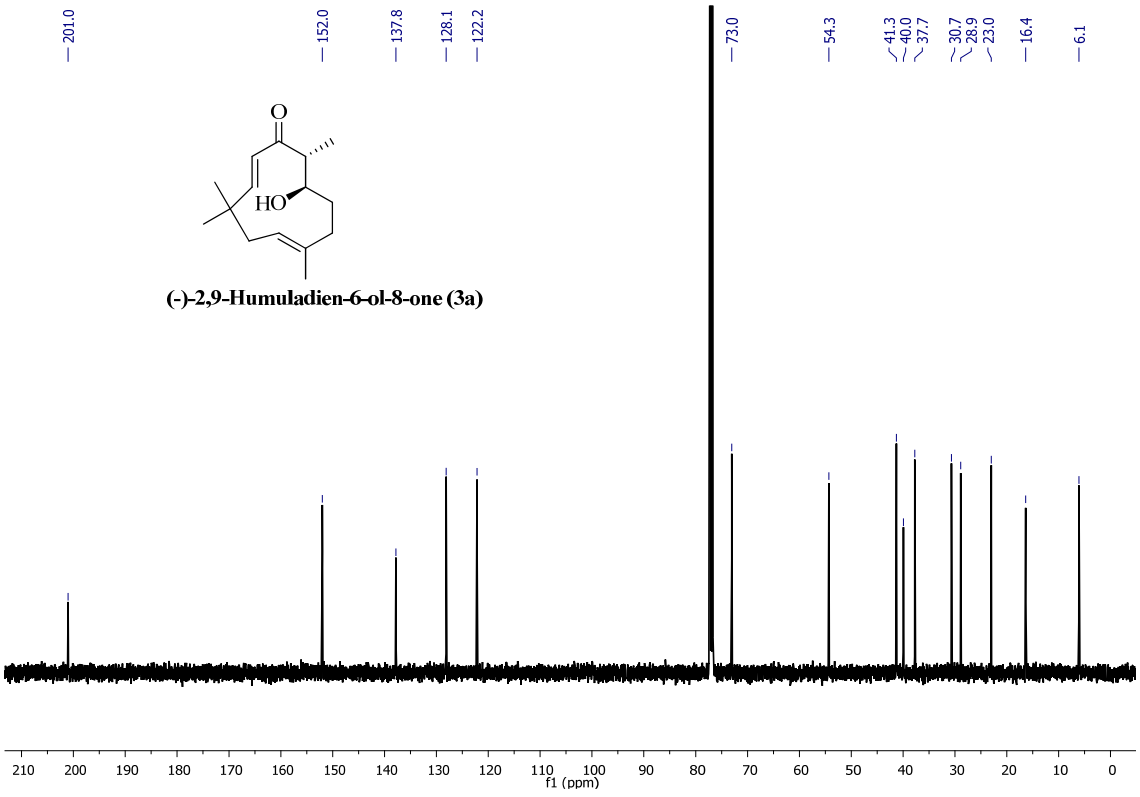


12. NMR, IR, X-ray, ECD, UV, HPLC of final compounds.

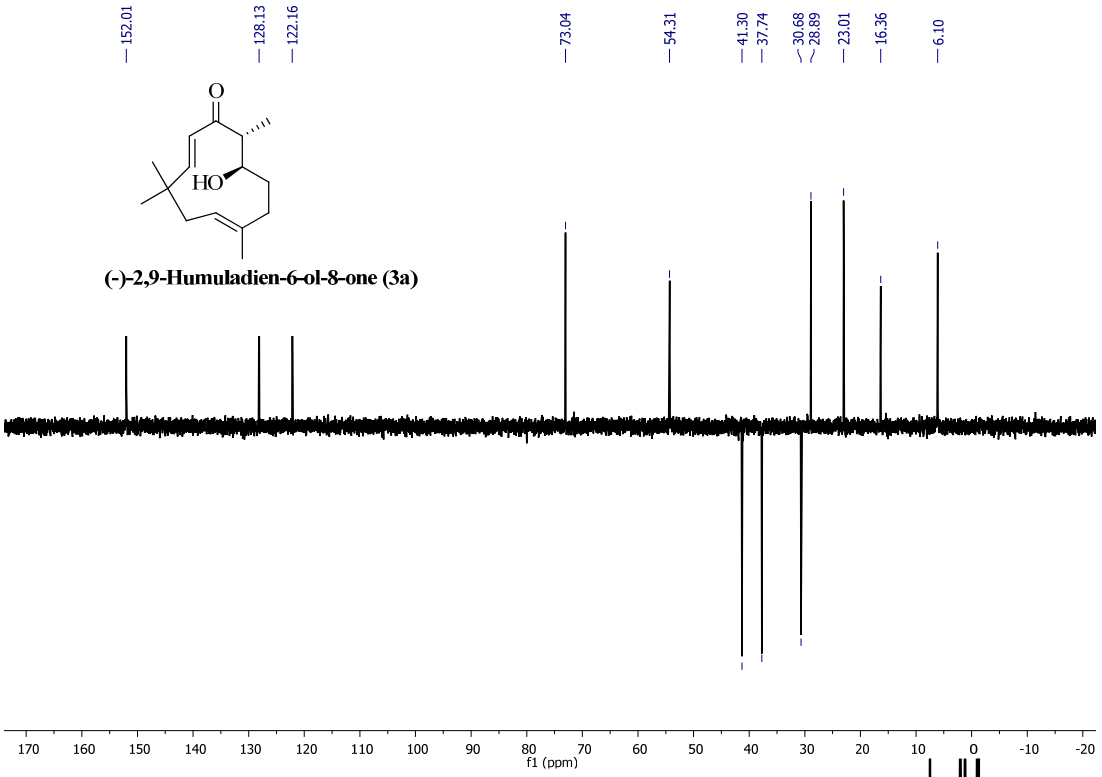
12.1. ^{1}H NMR of compound (-)-2,9-Humuladien-6-ol-8-one (3a) (500MHz, $CDCl_3$)



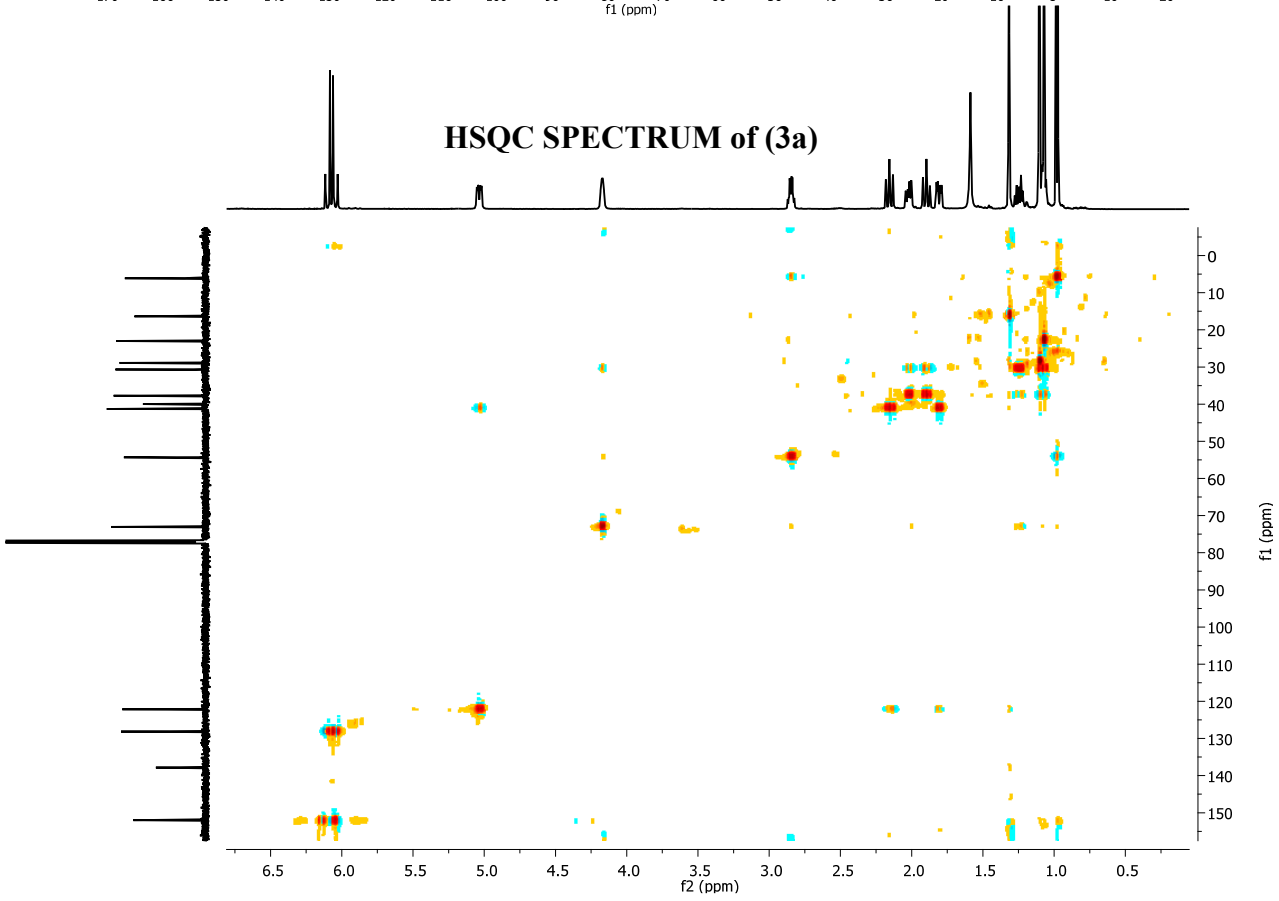
12.1. ^{13}C NMR of compound (-)-2,9-Humuladien-6-ol-8-one (3a) (125MHz, $CDCl_3$)



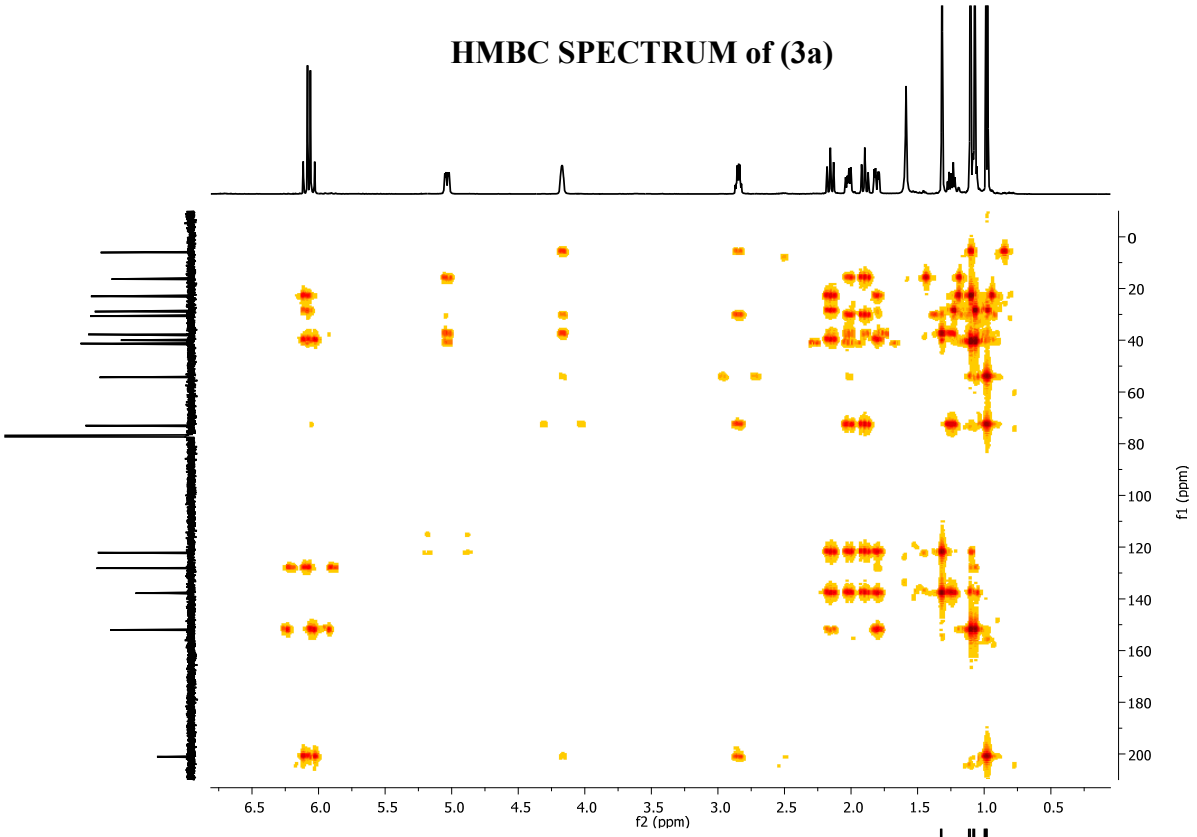
12.1. DEPT-135 NMR of compound (-)-2,9-Humuladien-6-ol-8-one (3a) (125MHz, $CDCl_3$)



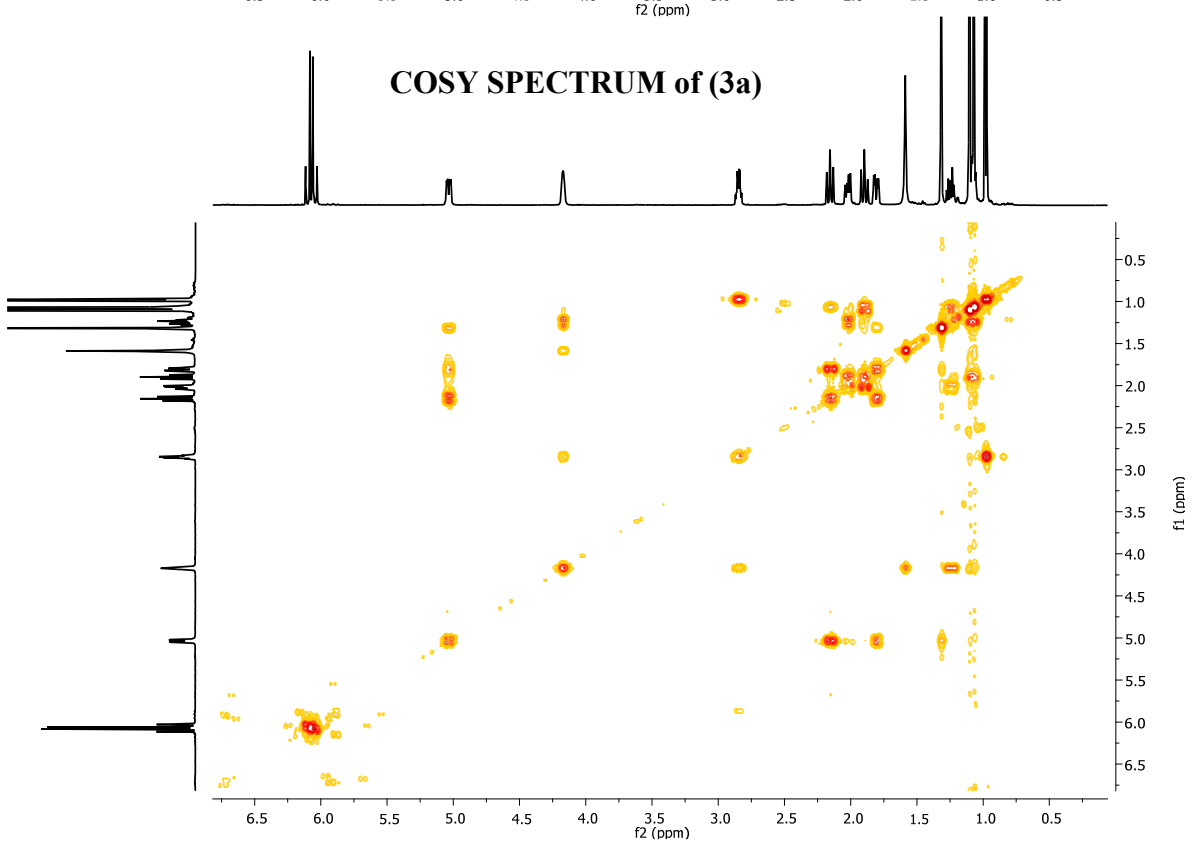
HSQC SPECTRUM of (3a)



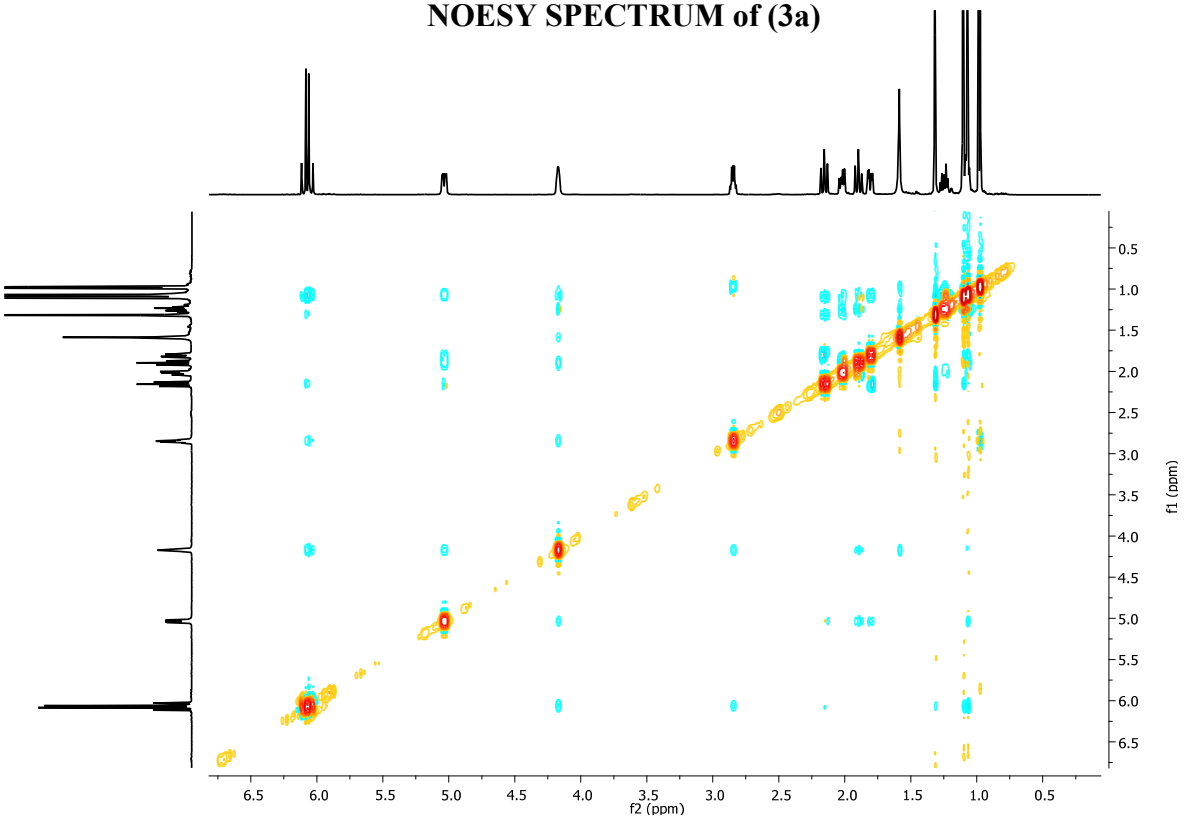
HMBC SPECTRUM of (3a)



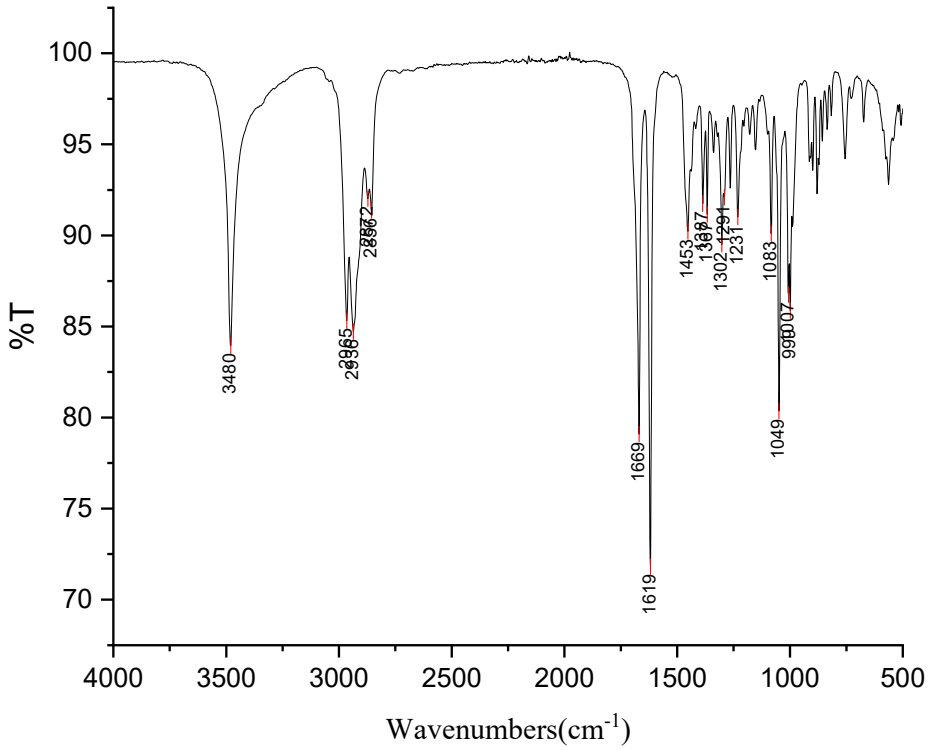
COSY SPECTRUM of (3a)



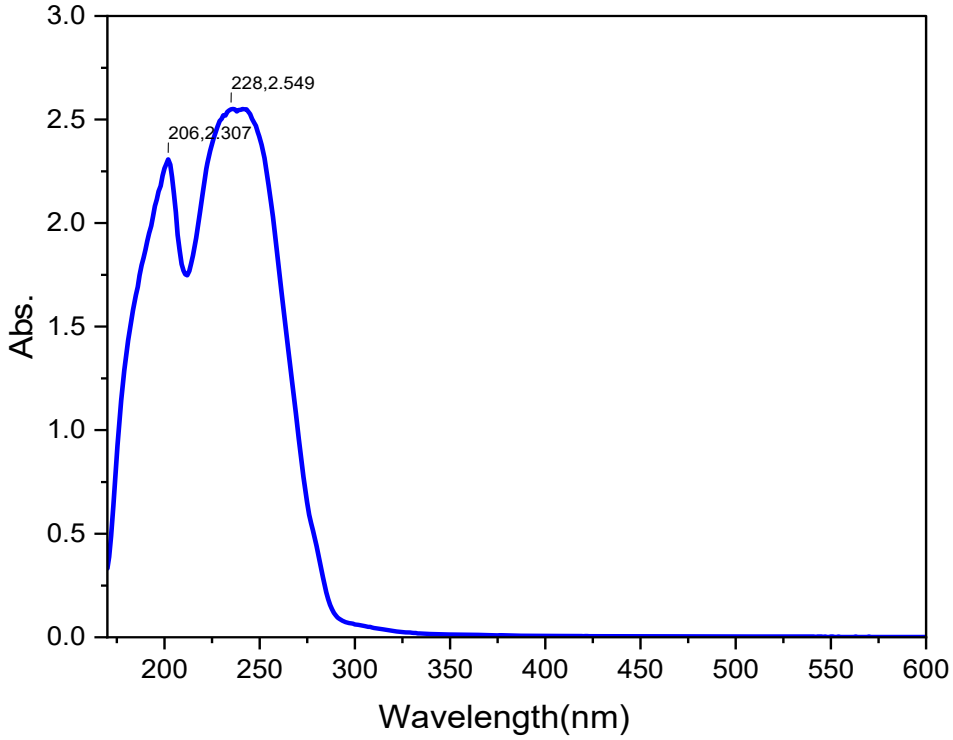
NOESY SPECTRUM of (3a)



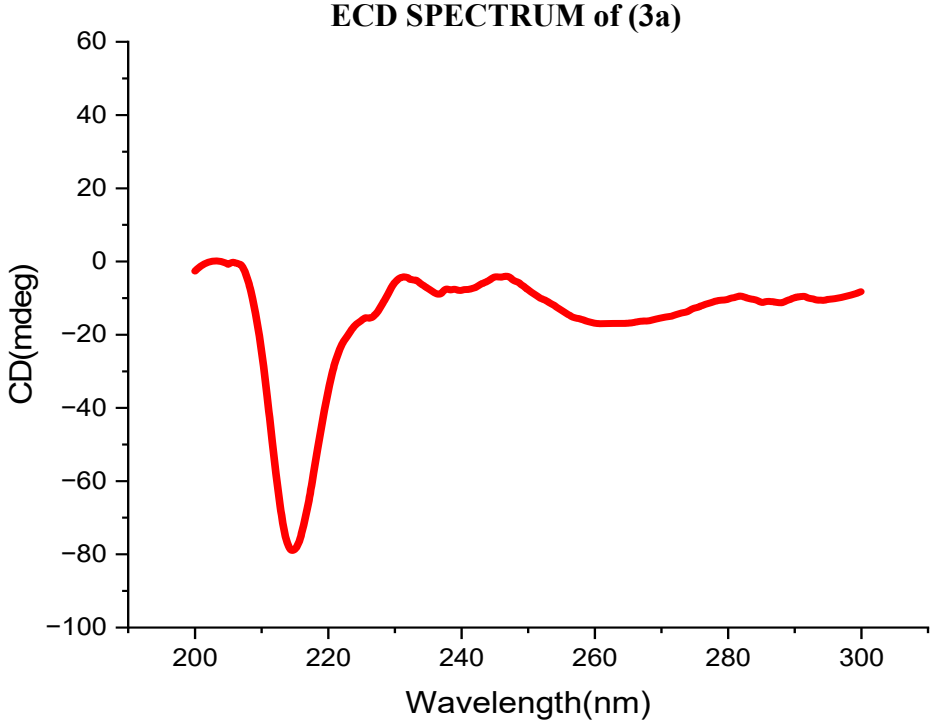
IR SPECTRUM of (3a)



UV SPECTRUM of (3a)



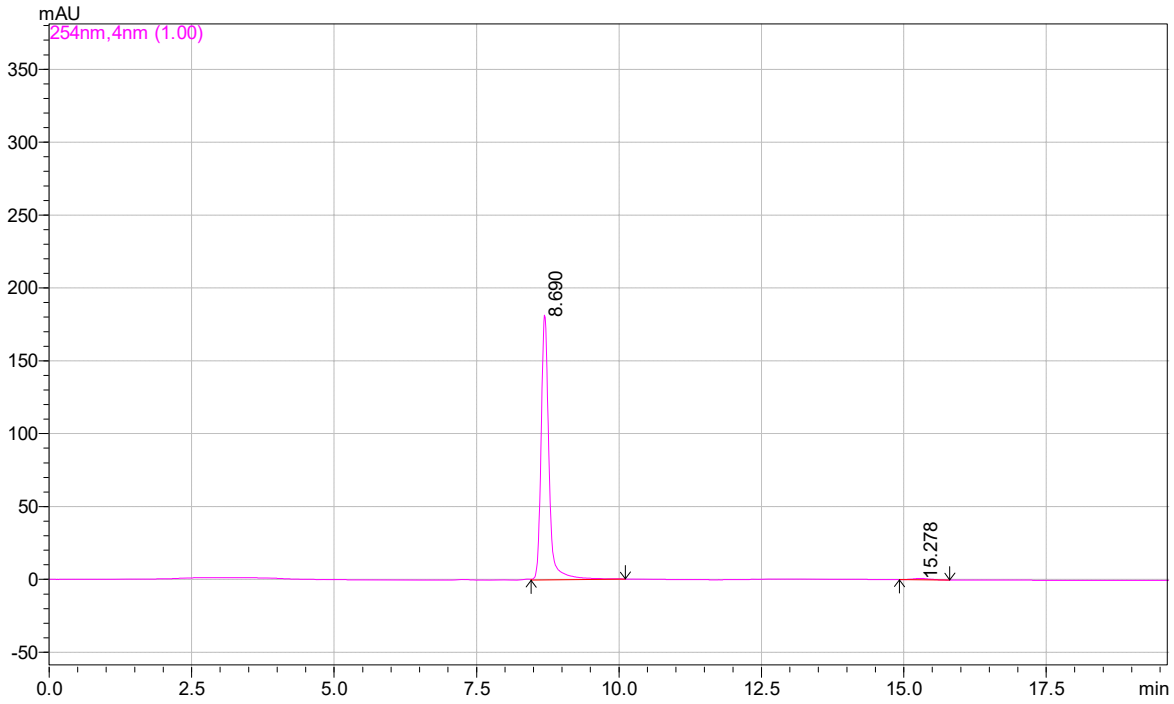
ECD SPECTRUM of (3a)



HPLC of (-)-2,9-Humuladien-6-ol-8-one (3a)

Column: CHIRALPAK OJ; Flow rate: 1.0 ml/min

Mobile phase: 10:1; hexane:IPA; Injection volume: 10µl.

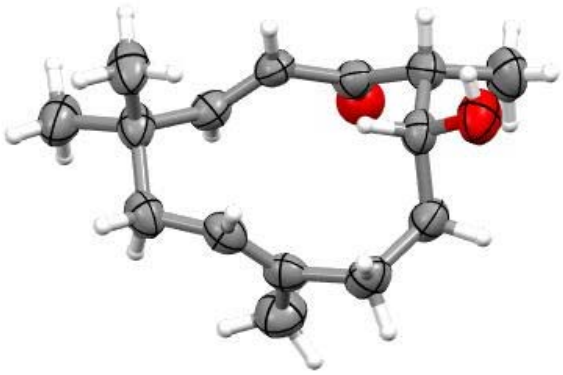


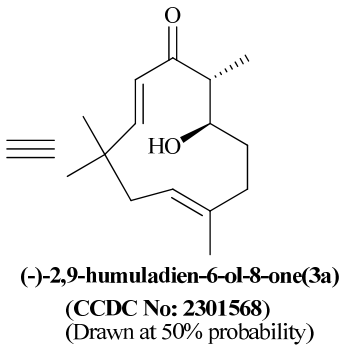
PDA Ch1 254nm 4nm

Peak#	Ret time	Conc	area	Height	Area (%)
1	8.690	98.78736	1746317	181698	98.78736
2	15.278	1.21264	21437	948	1.21264

Crystal data and structure refinement for compound (3a)

X-ray crystal data of compound **3a** (the following crystal has been deposited at the Cambridge Crystallographic Data Centre and has the deposition number **(CCDC No: 2301568).**





(-)-2,9-humuladien-6-ol-8-one(3a)
(CCDC No: 2301568)
(Drawn at 50% probability)

Bond precision: C-C = 0.0029 A Wavelength=0.71073

Cell: a=6.0794(2) b=13.0587(4) c=17.7262(6)
alpha=90 beta=90 gamma=90

Temperature: 296 K

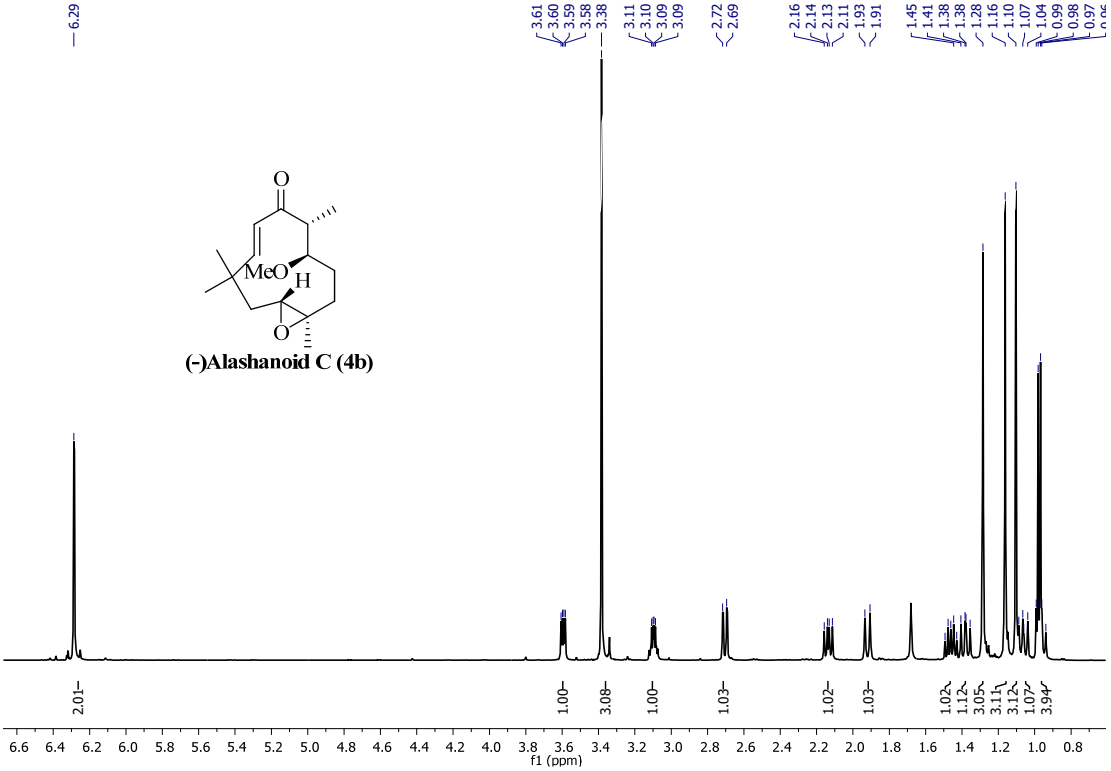
	Calculated	Reported
Volume	1407.27(8)	1407.27(8)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2xab;2ybc
Moiety formula	C15 H24 O2	?
Sum formula	C15 H24 O2	C15 H24 O2
Mr	236.34	236.40
Dx,g cm-3	1.115	1.116
Z	4	4
Mu (mm-1)	0.072	0.072
F000	520.0	520.0
F000'	520.23	
h,k,lmax	7,16,22	7,16,22
Nref	3108[1811]	3092
Tmin,Tmax	0.999,0.999	0.707,0.746
Tmin'	0.999	

Correction method= # Reported T Limits: Tmin=0.707 Tmax=0.746 AbsCorr = MULTI-SCAN

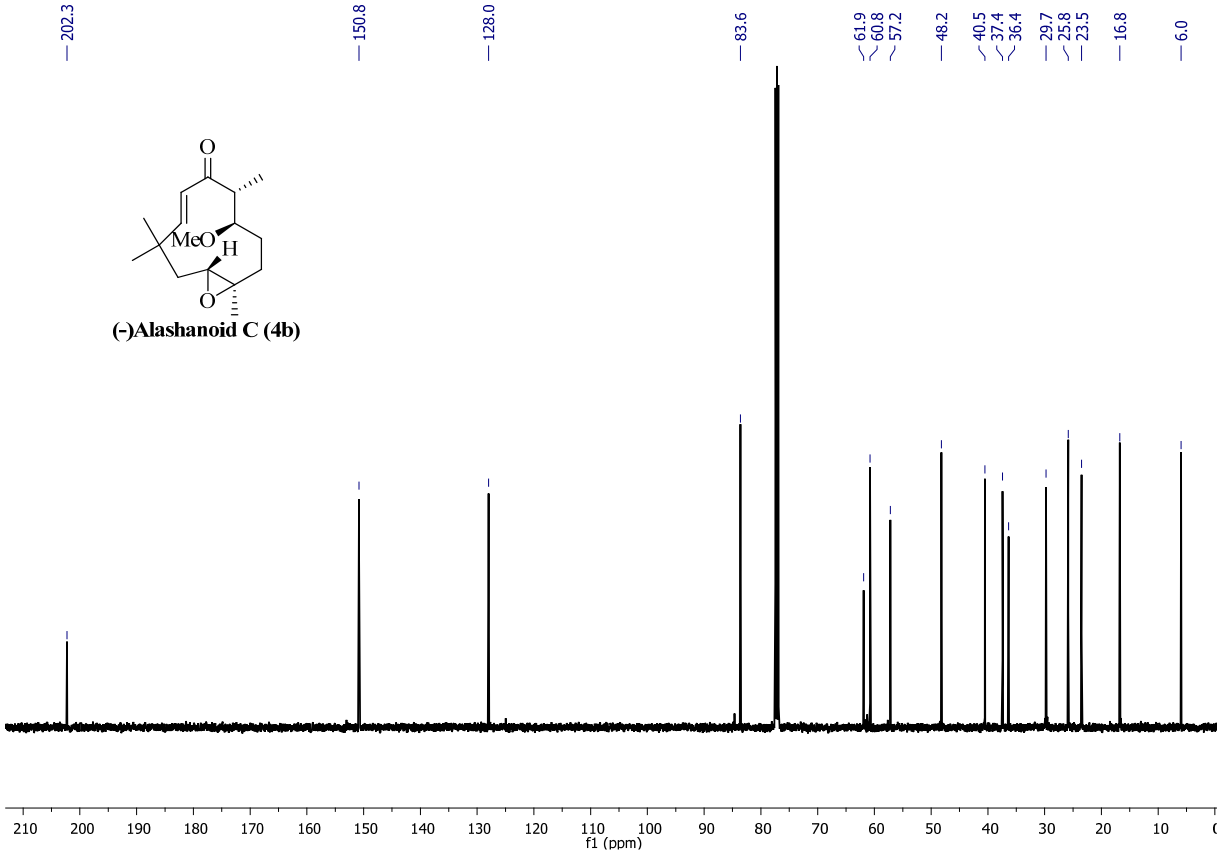
Data completeness= 1.71/0.99 Theta(max)= 27.100

R(reflections)= 0.0463(2640) wR2(reflections)= wR= 0.0552(3092)

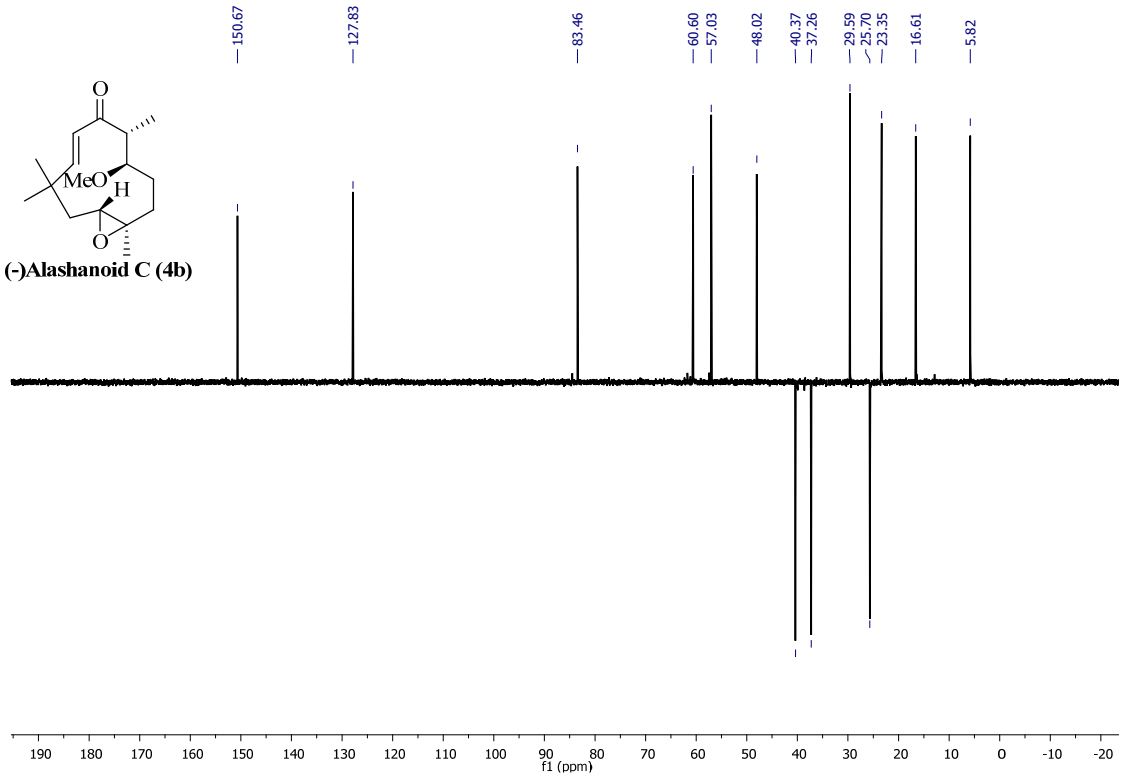
12.2: ^{1}H NMR of (-)-alashanoid C (4b) (500MHz, $CDCl_3$)

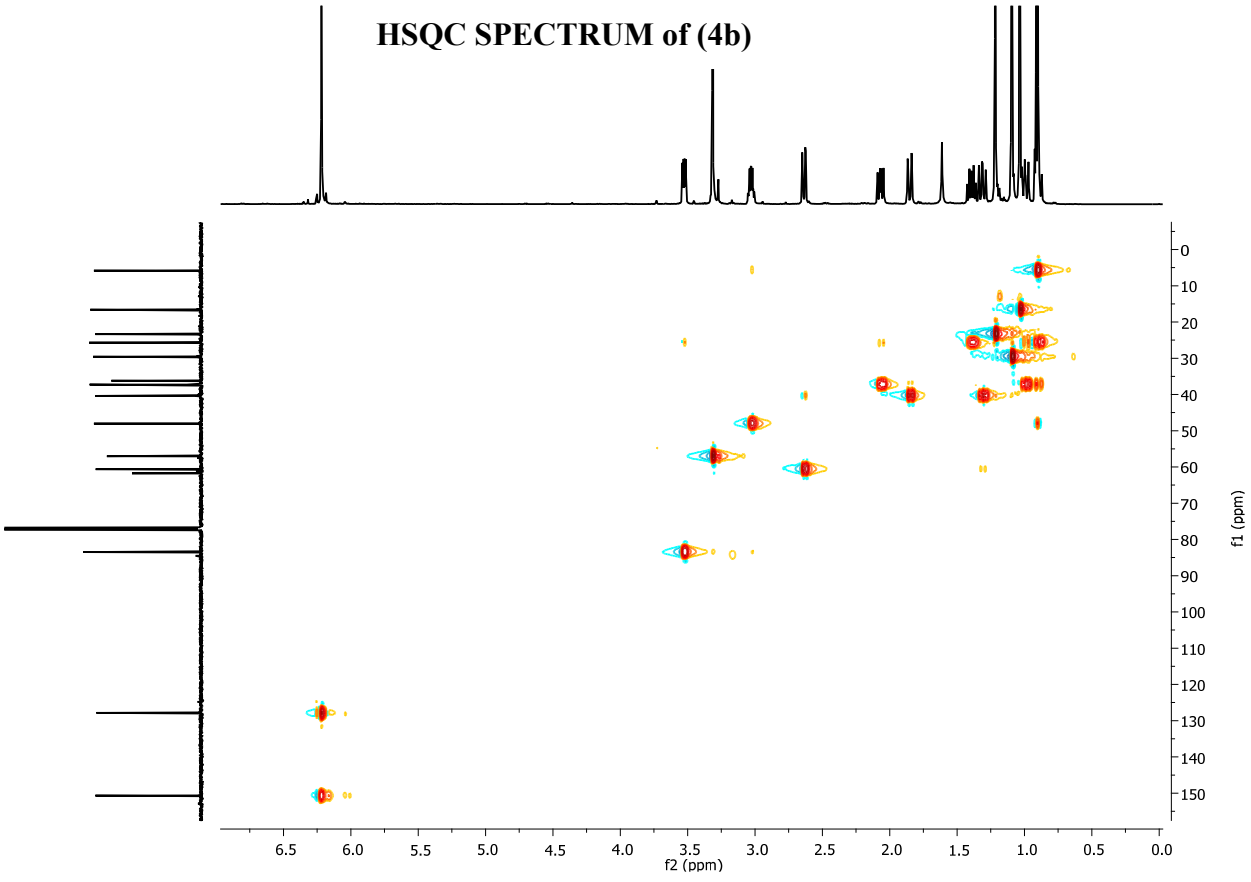


12.2: ^{13}C NMR of (-)-alashanoid C (4b) (125MHz, $CDCl_3$)

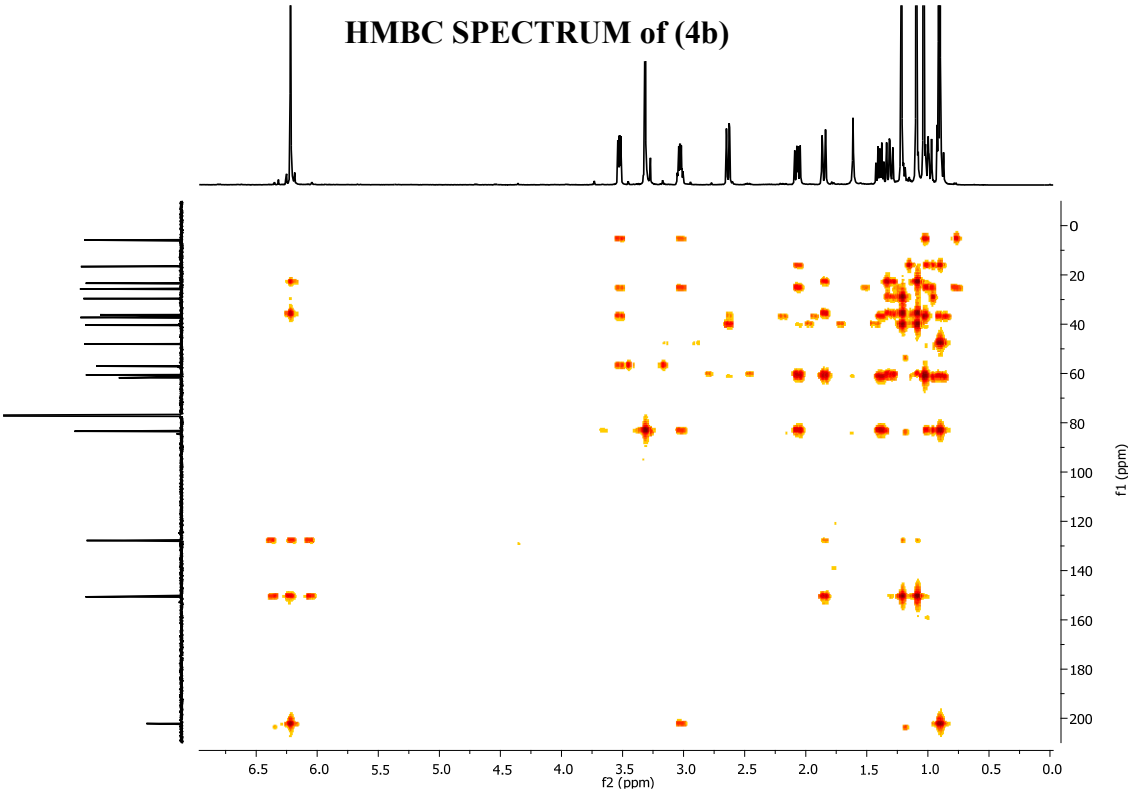


12.2: DEPT-135 NMR of (-)-alashanoid C (4b) (125MHz, $CDCl_3$):

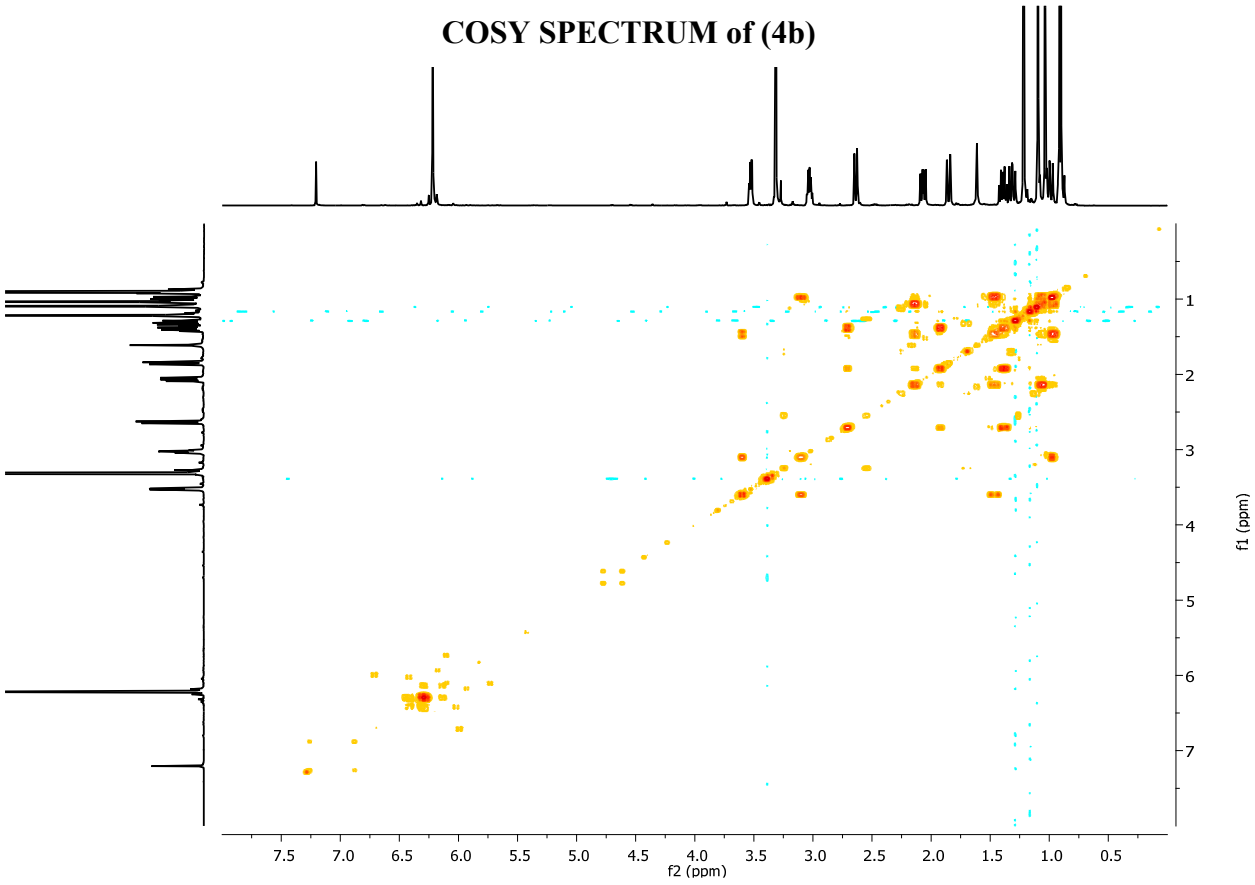




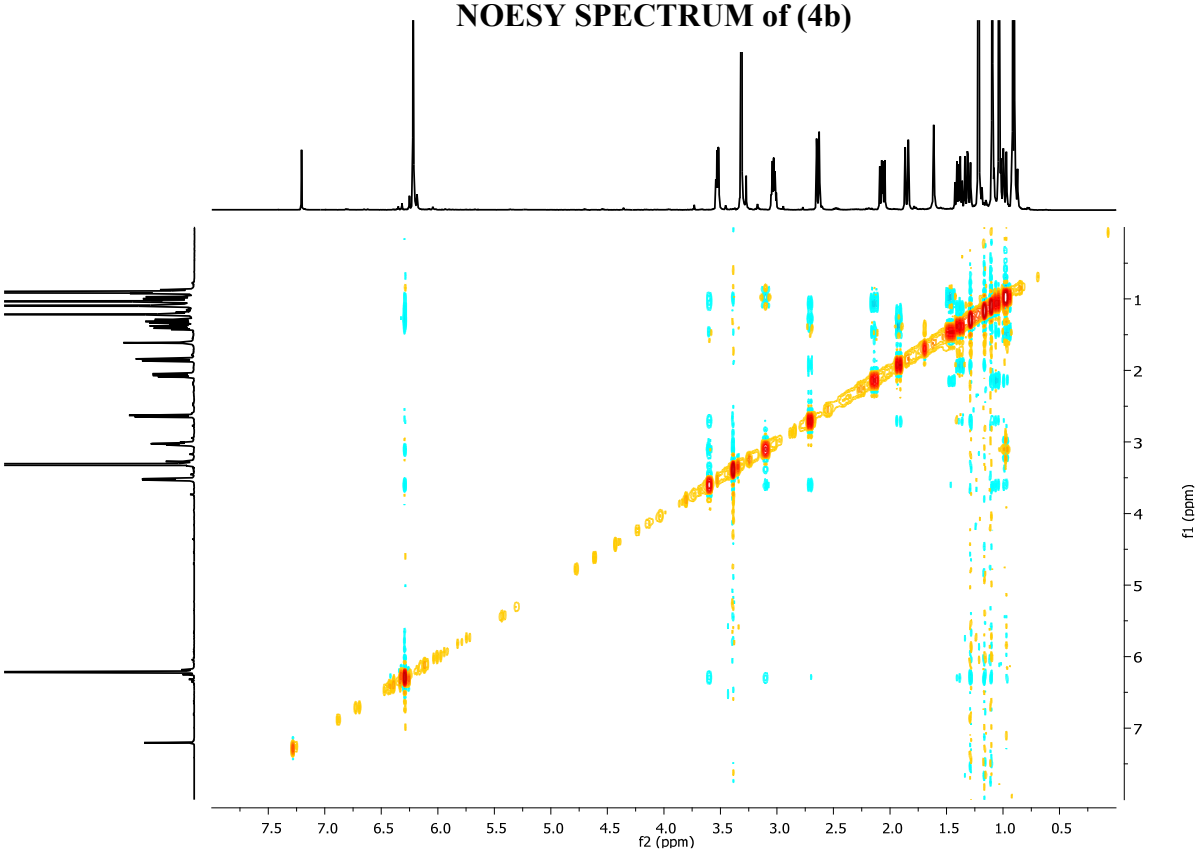
HMBC SPECTRUM of (4b)



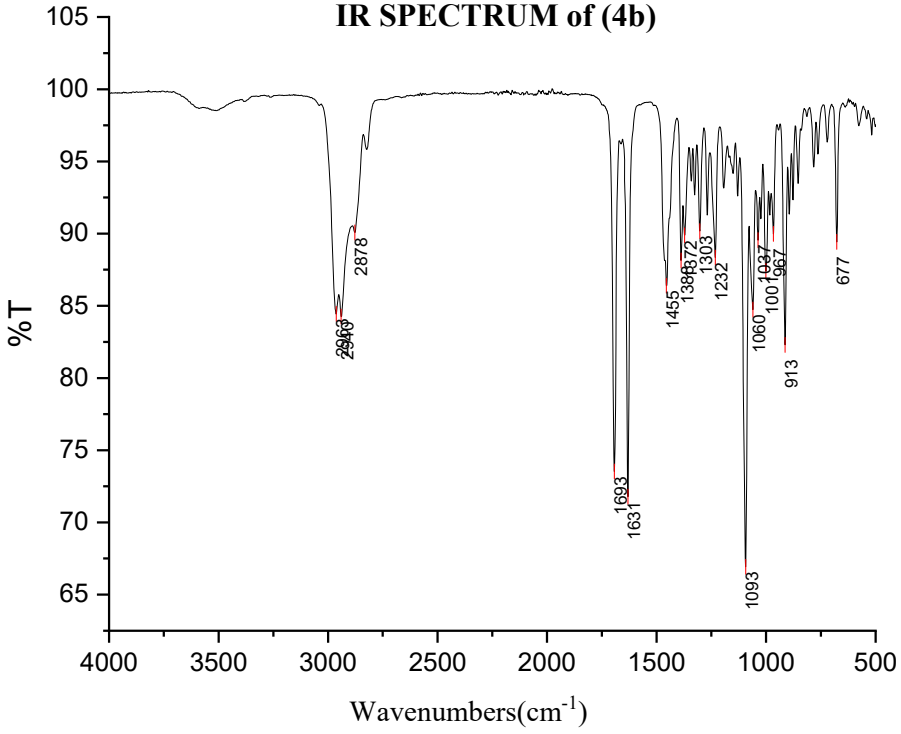
COSY SPECTRUM of (4b)



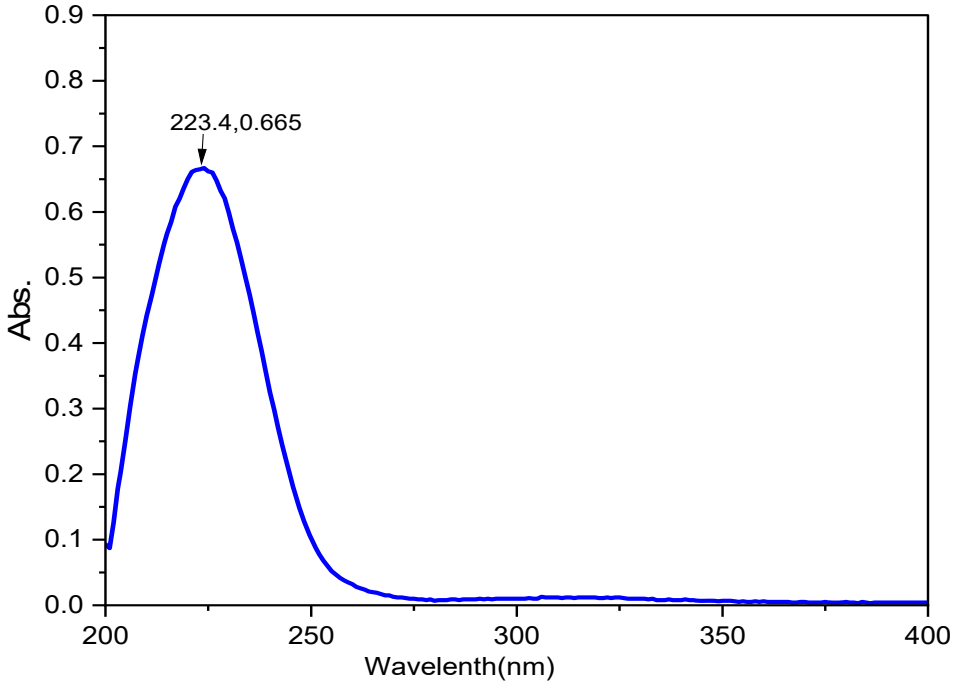
NOESY SPECTRUM of (4b)



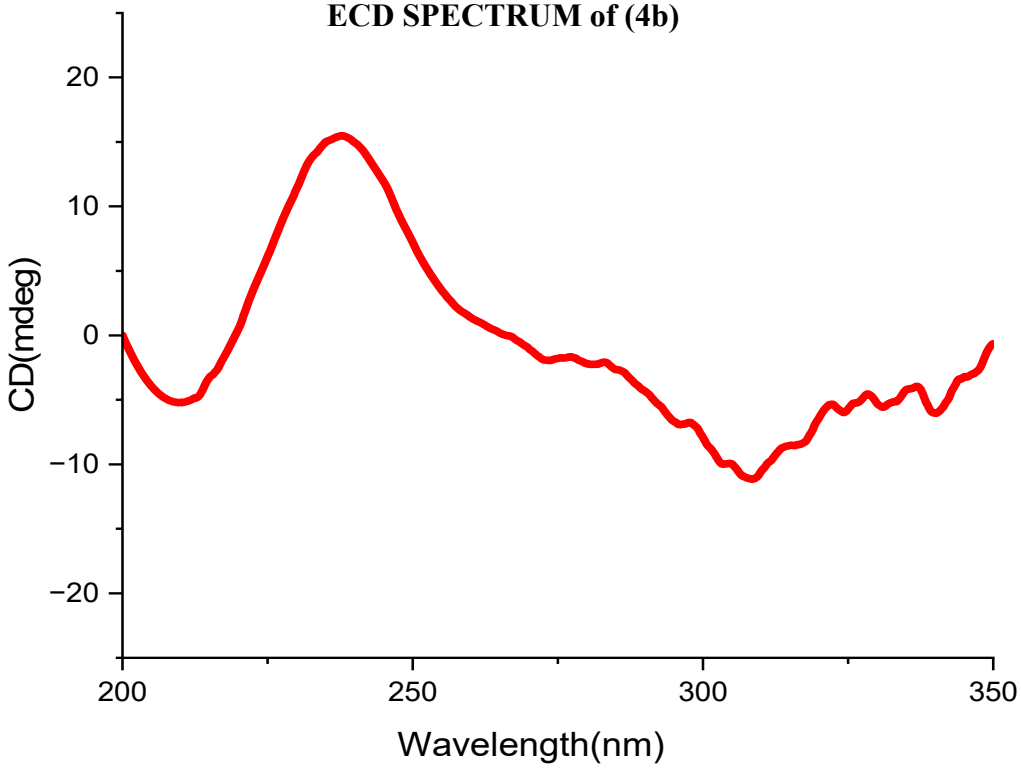
IR SPECTRUM of (4b)



UV SPECTRUM of (4b)



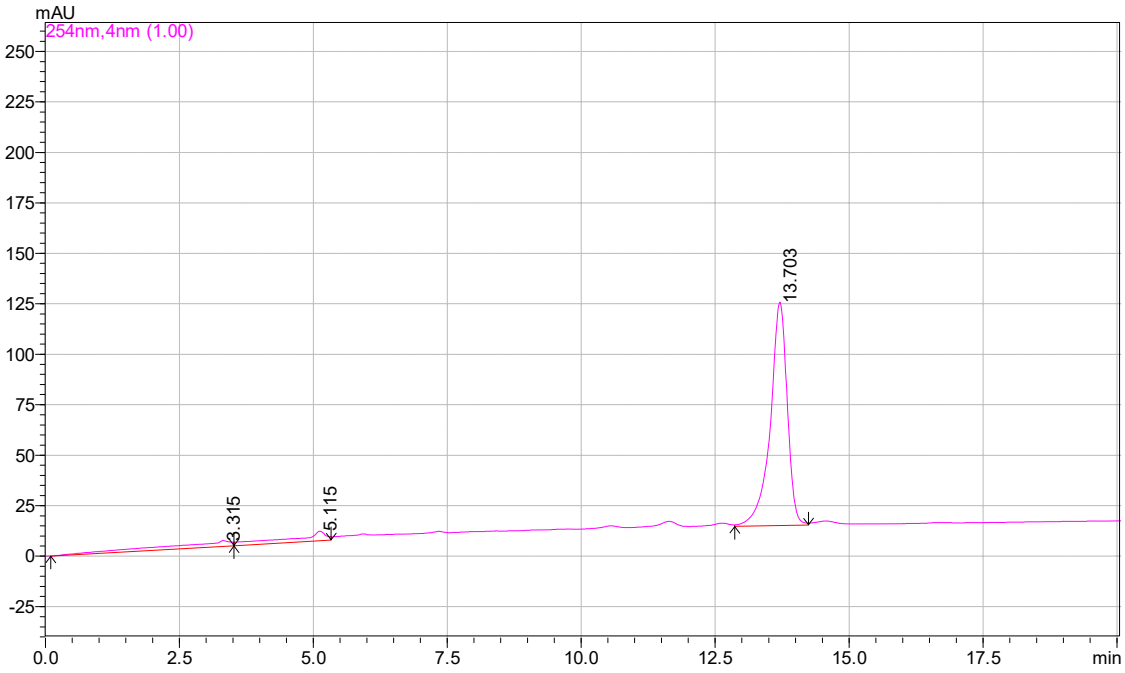
ECD SPECTRUM of (4b)



HPLC of (-)-alashanoid C (4b)

Column: CHIRALPAK OJ; Flow rate: 1.0 ml/min

Mobile phase: 10:1; hexane:IPA; Injection volume: 10µL

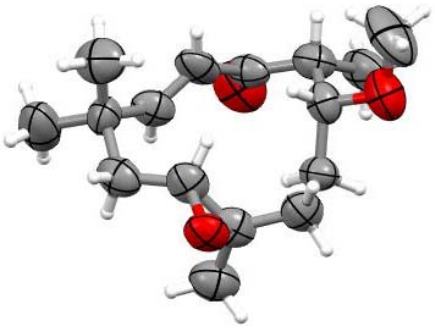


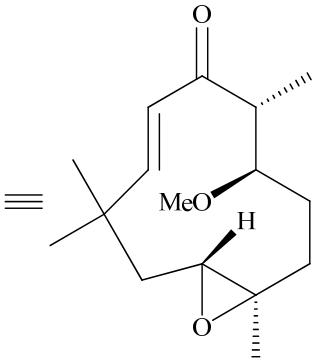
PDA Ch1 254nm 4nm

Peak#	Ret time	Conc	area	Height	Area (%)
1	3.315	2.96958	262214	2839	2.96958
2	5.115	3.57188	221354	4772	3.57188
3	13.703	93.45854	2439802	110651	93.45854

Crystal data and structure refinement for compound (4b)

X-ray crystal data of compound **4b** (the following crystal has been deposited at the Cambridge Crystallographic Data Centre and has the deposition number **(CCDC No: 2305842).**





(-)Alashanoid C (4b) (CCDC No: 2305842)
(Drawn at 30% probability)

Bond precision: C-C = 0.0143 A Wavelength=0.71073

Cell: a=9.7763(12) b=14.2275(14) c=12.0706(16)
alpha=90 beta=107.436(14) gamma=90

Temperature: 298 K

	Calculated	Reported
Volume	1601.8(4)	1601.8(3)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C16 H26 O3	C16 H26 O3
Sum formula	C16 H26 O3	C16 H26 O3
Mr	266.37	266.37
Dx,g cm-3	1.105	1.105
Z	4	4
Mu (mm-1)	0.074	0.074
F000	584.0	584.0
F000'	584.27	
h,k,lmax		16,22,20
Nref		13876
Tmin,Tmax		0.345,1.000
Tmin'		

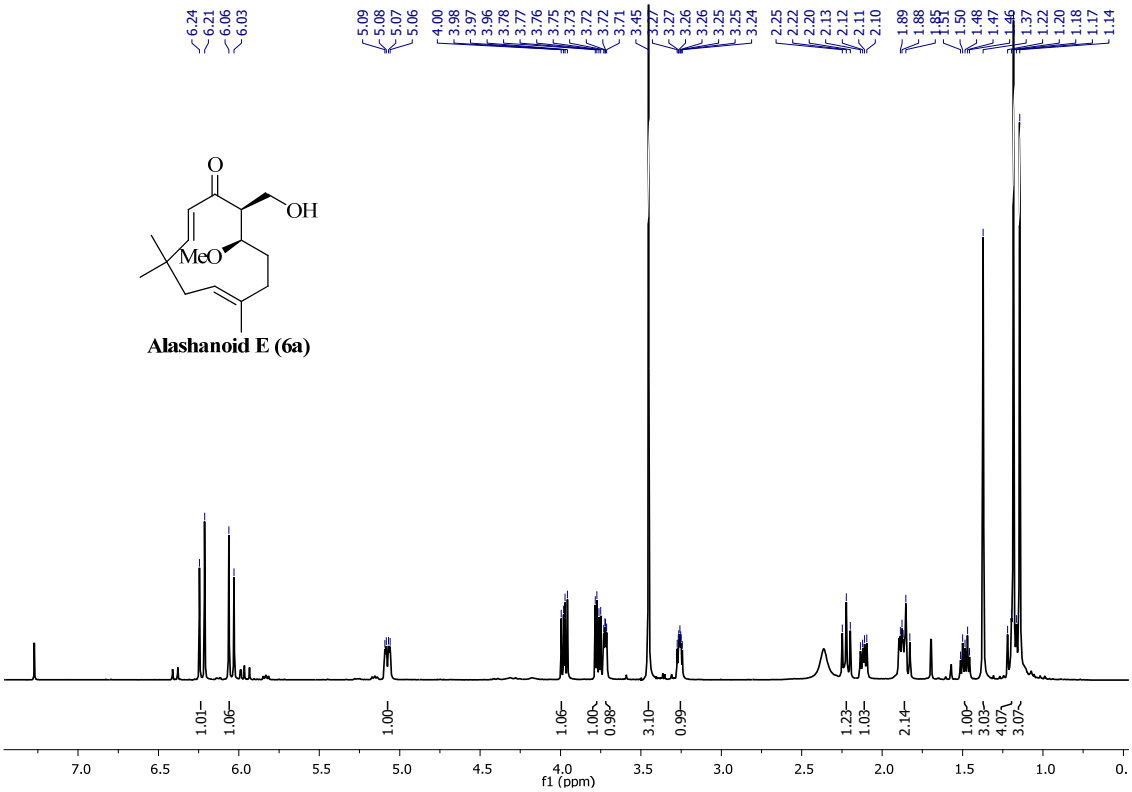
Correction method= # Reported T Limits: Tmin=0.345 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= Theta(max)= 38.284

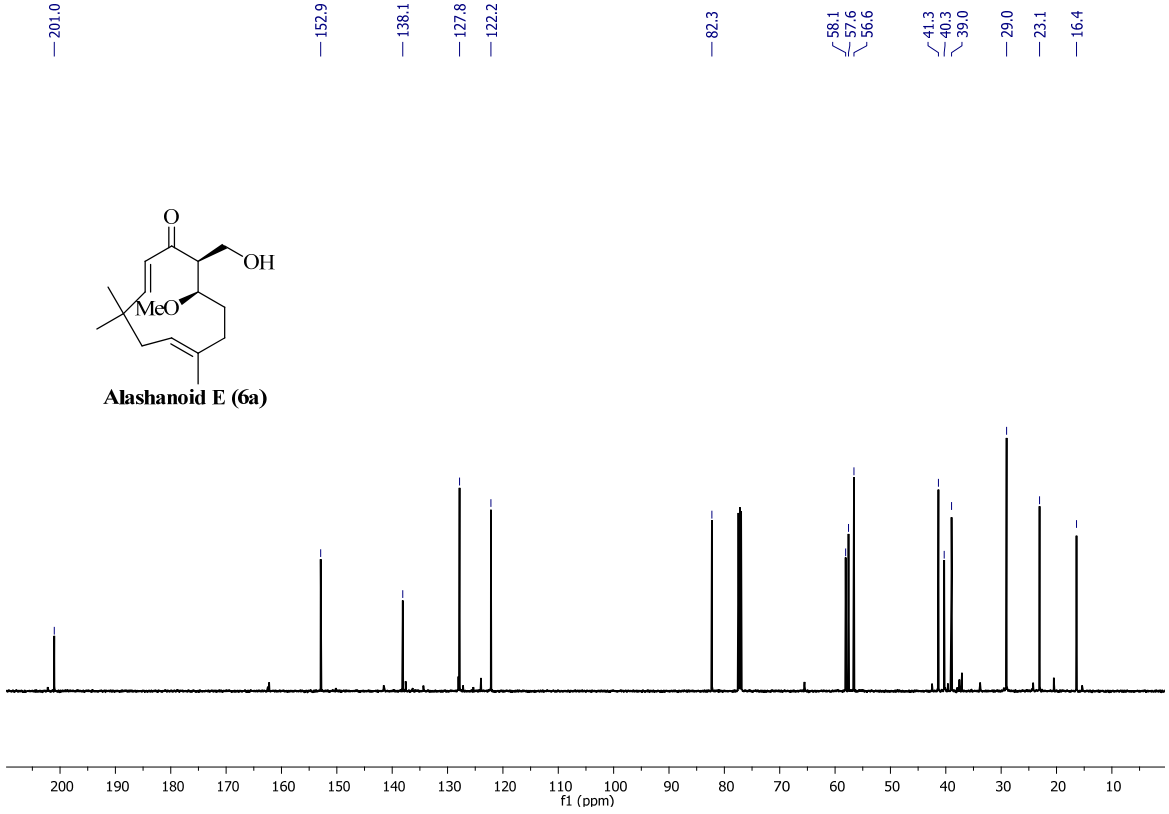
R(reflections)= 0.1640(3620) wR2(reflections)= 0.4664(13876)

S = 0.994 Npar= 353

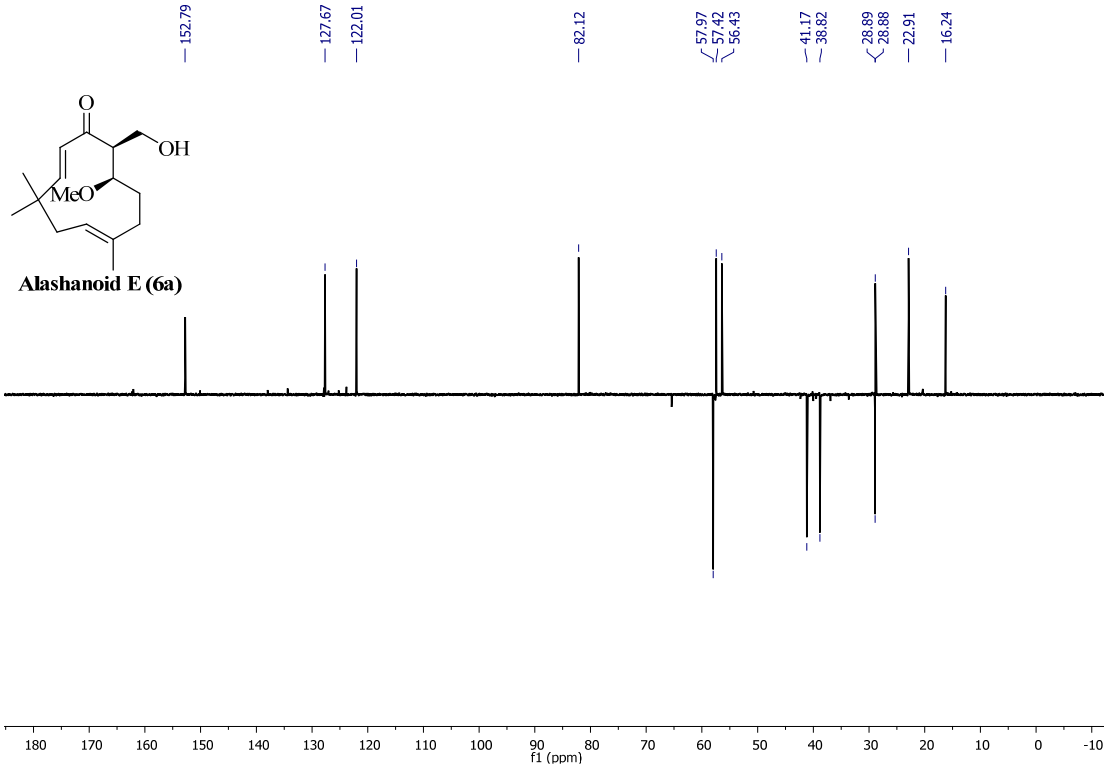
12.3: ^{1}H NMR of (+)-alashanoid E (6a) (500MHz, $CDCl_3$)

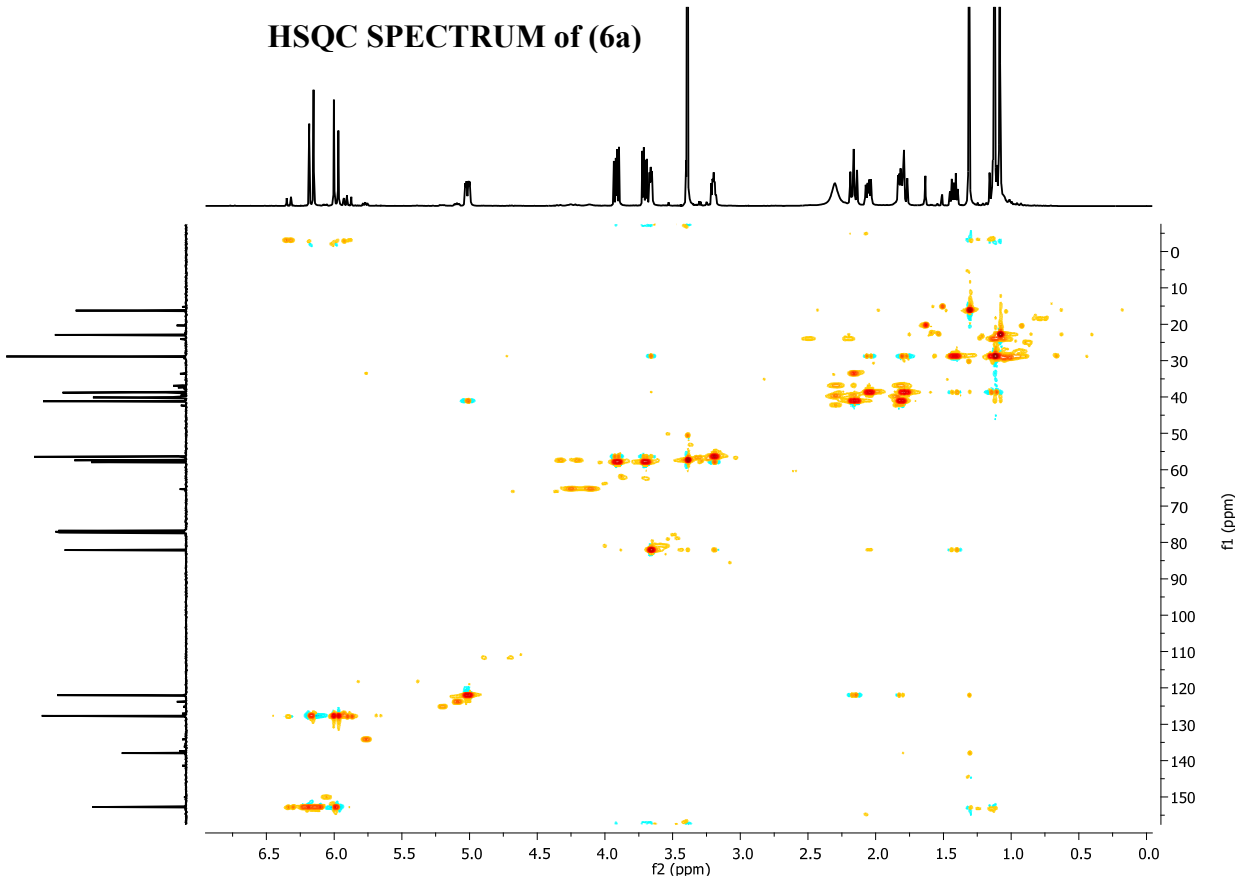


12.3: ^{13}C NMR of (+)-alashanoid E (6a) (125MHz, $CDCl_3$)

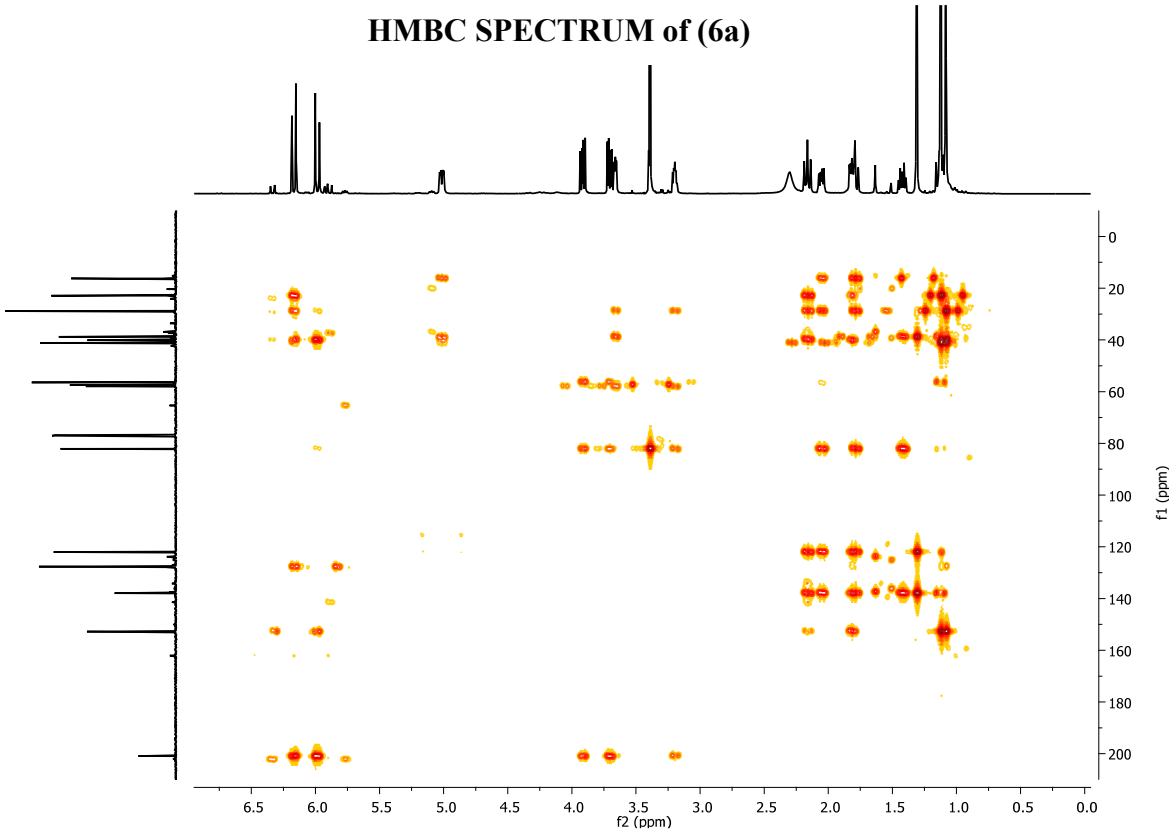


12.3: DEPT-135 NMR of (+)-alashanoid E (6a) (125MHz, $CDCl_3$)

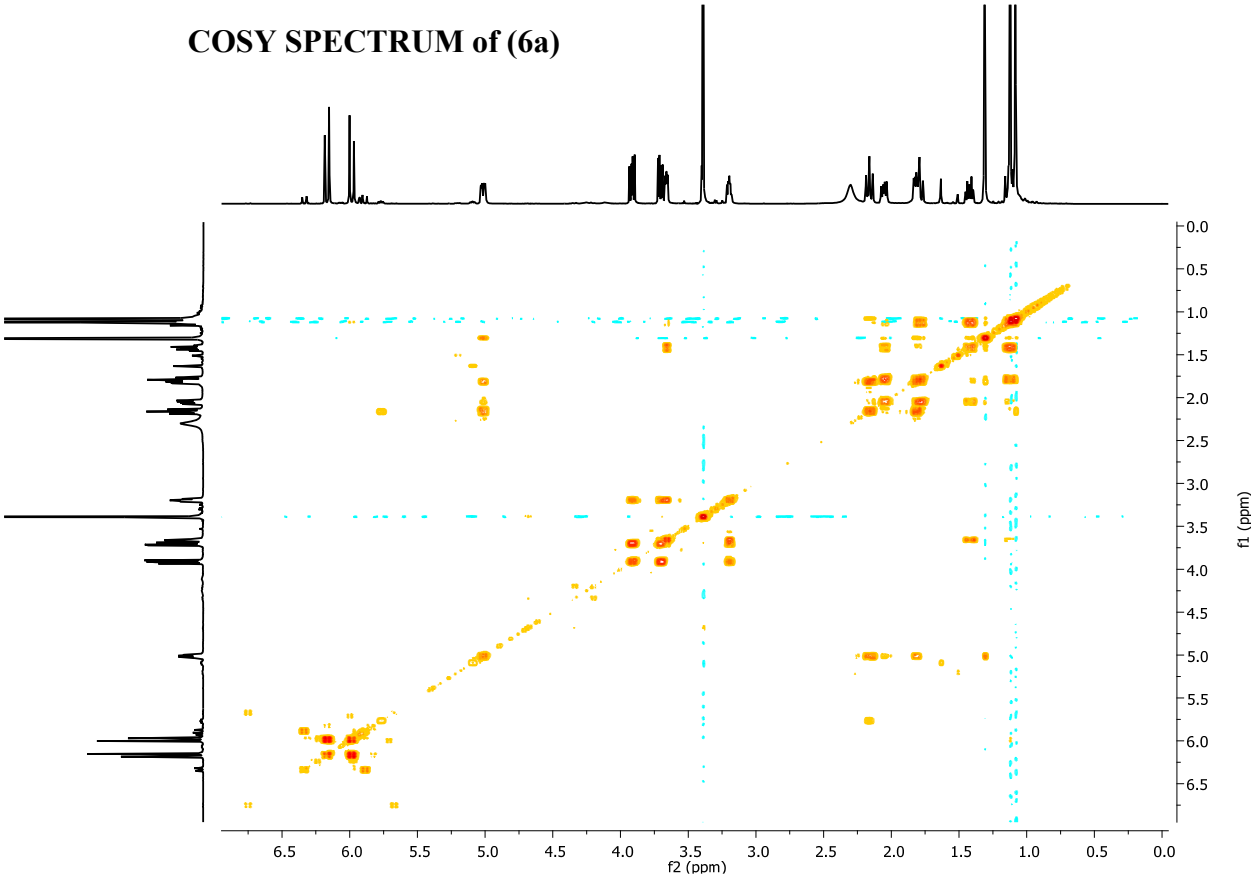




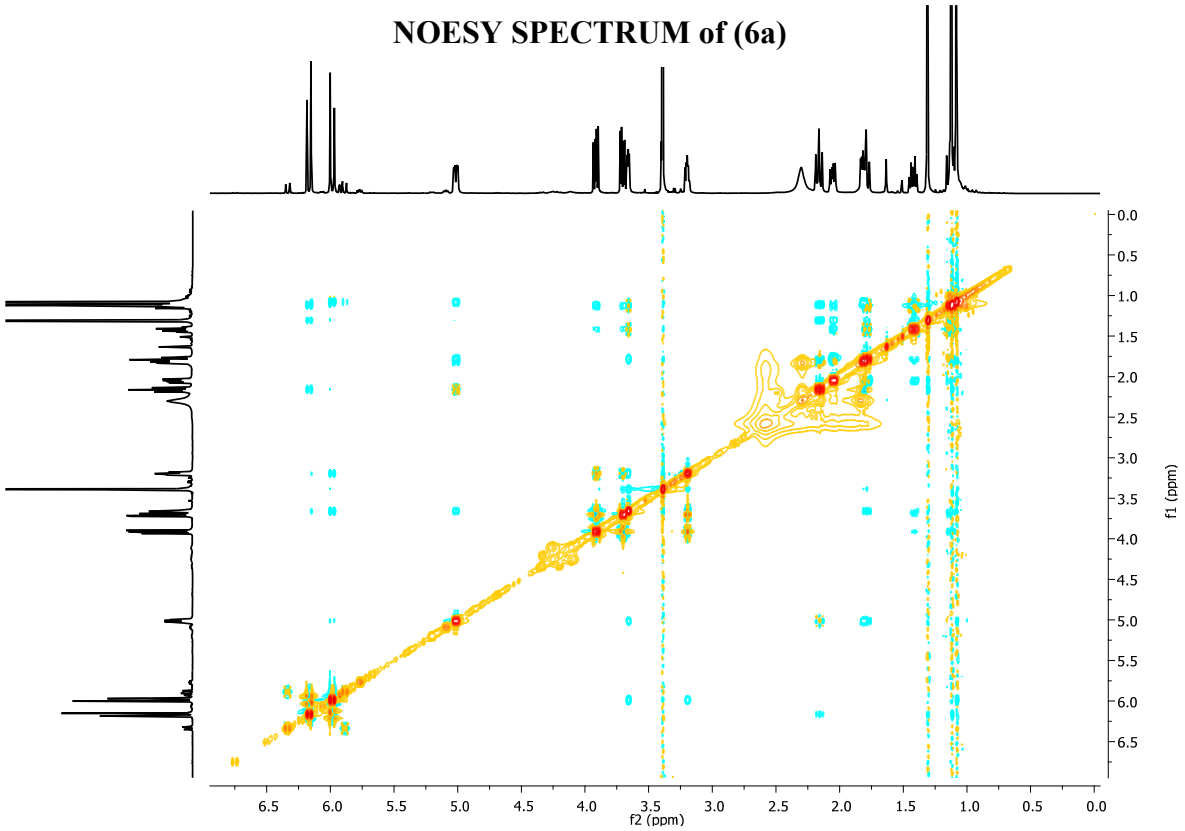
HMBC SPECTRUM of (6a)



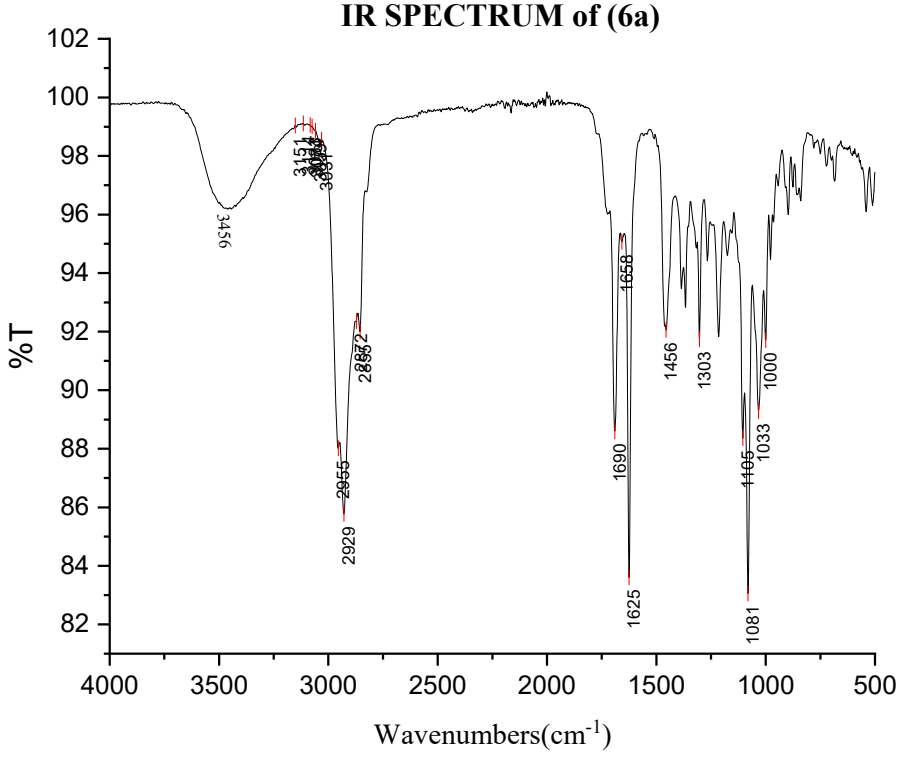
COSY SPECTRUM of (6a)



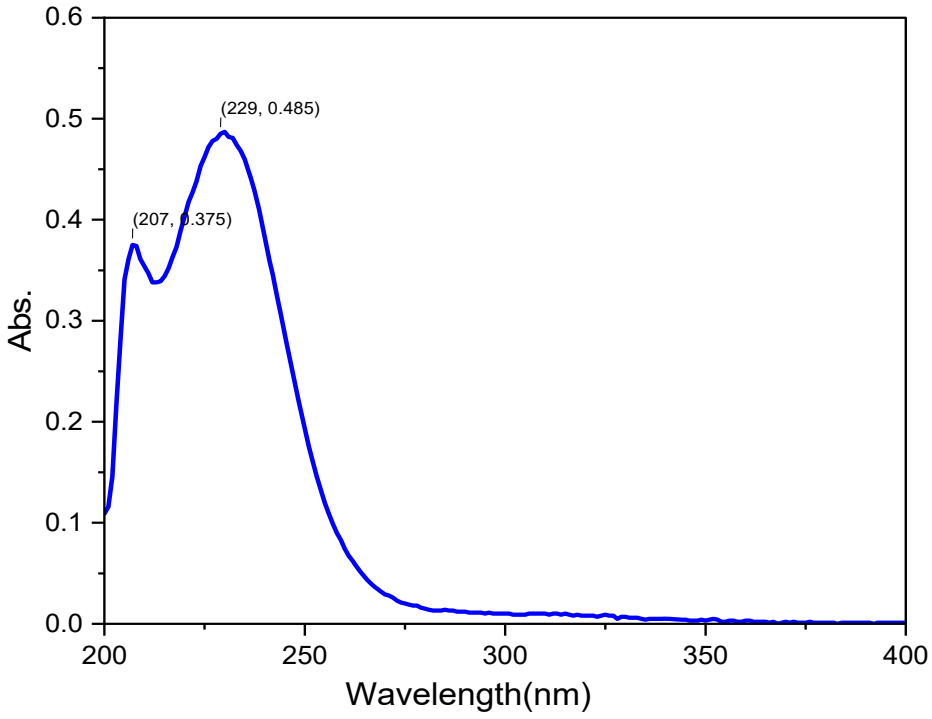
NOESY SPECTRUM of (6a)



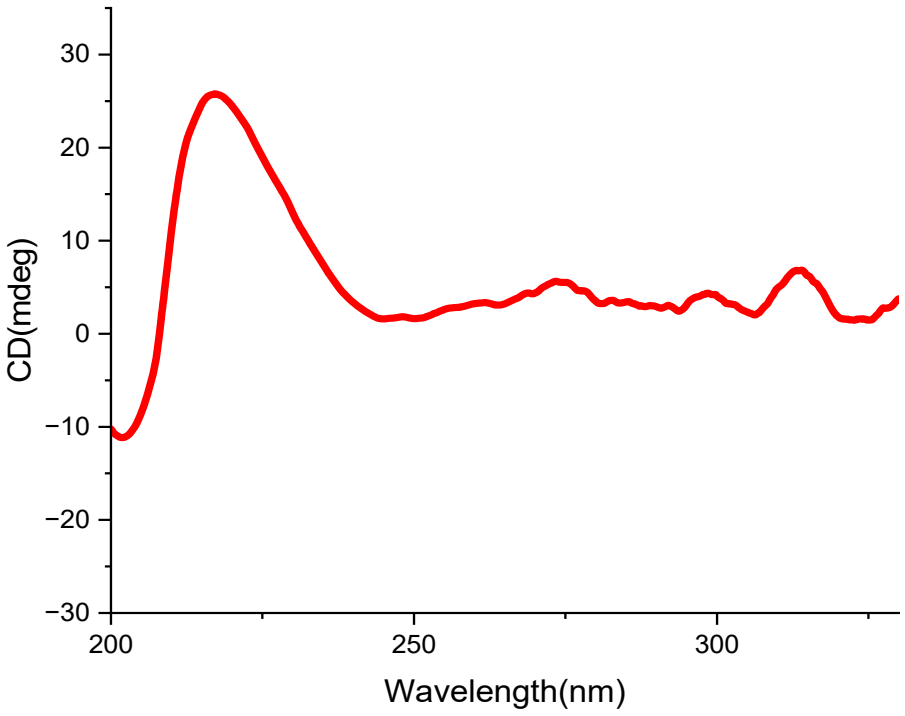
IR SPECTRUM of (6a)



UV SPECTRUM of (6a)



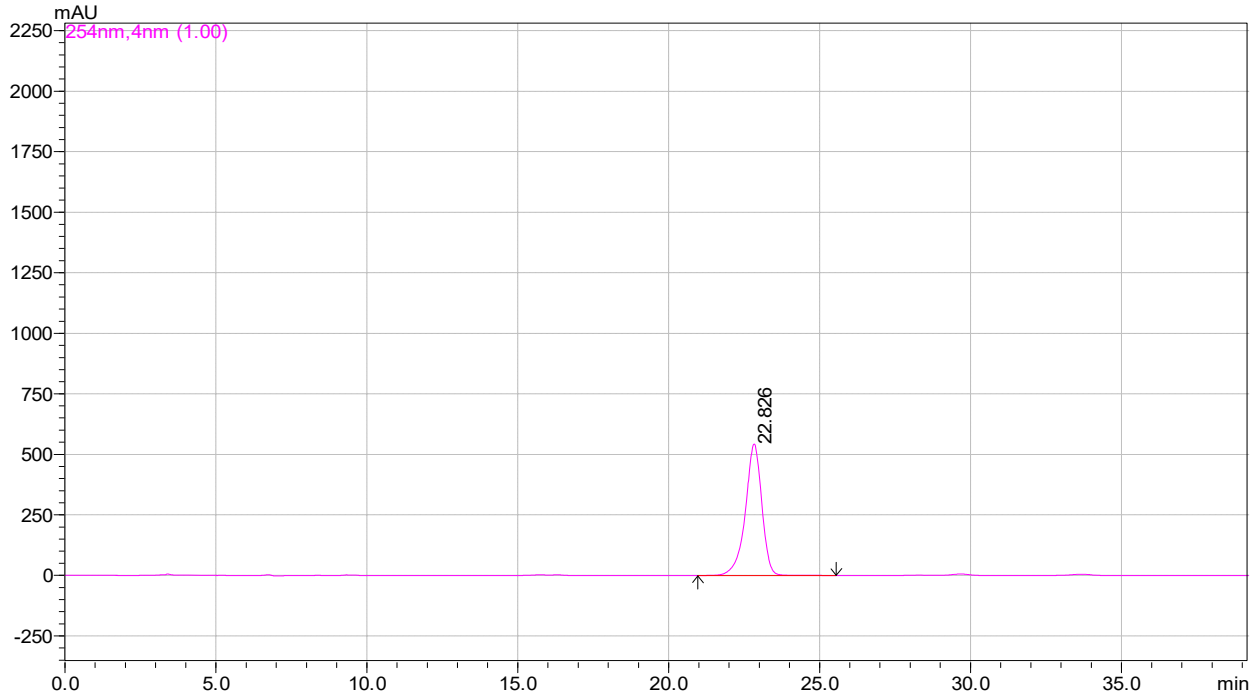
ECD SPECTRUM of (6a)



HPLC of (+)-alashanoid E(6a)

Column: CHIRALCEL IC; Flow rate: 0.8 ml/min

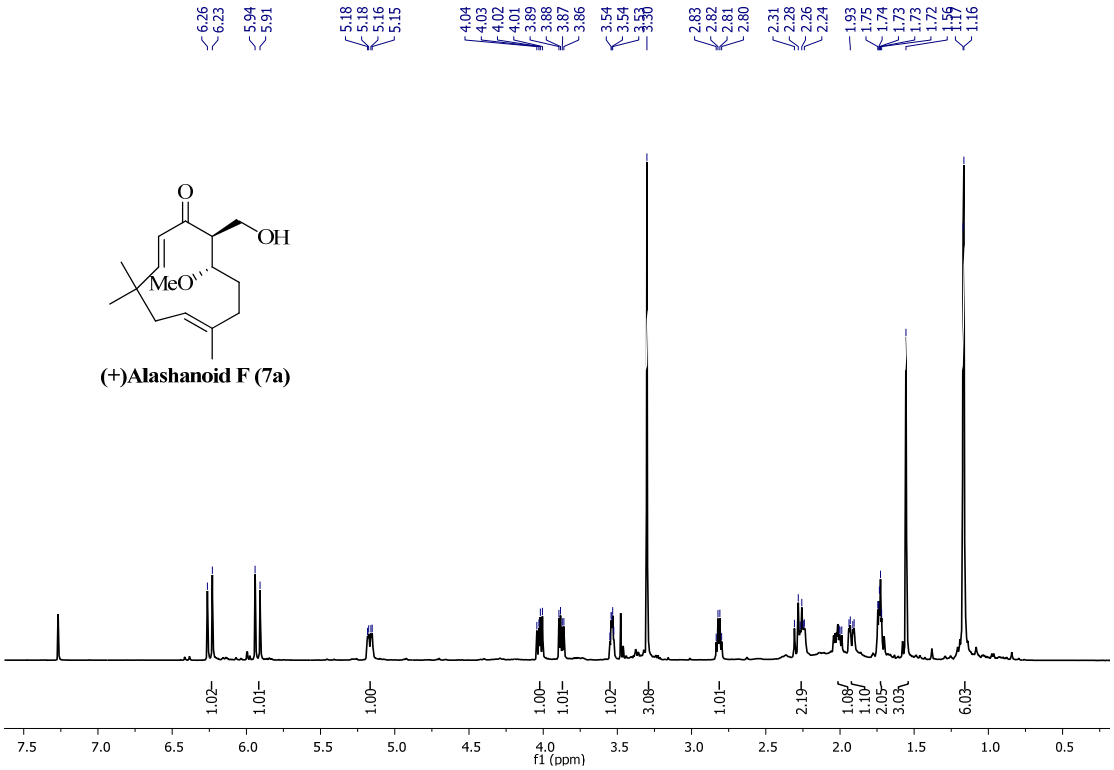
Mobile phase: 10:1; hexane:IPA; Injection volume: 10µL



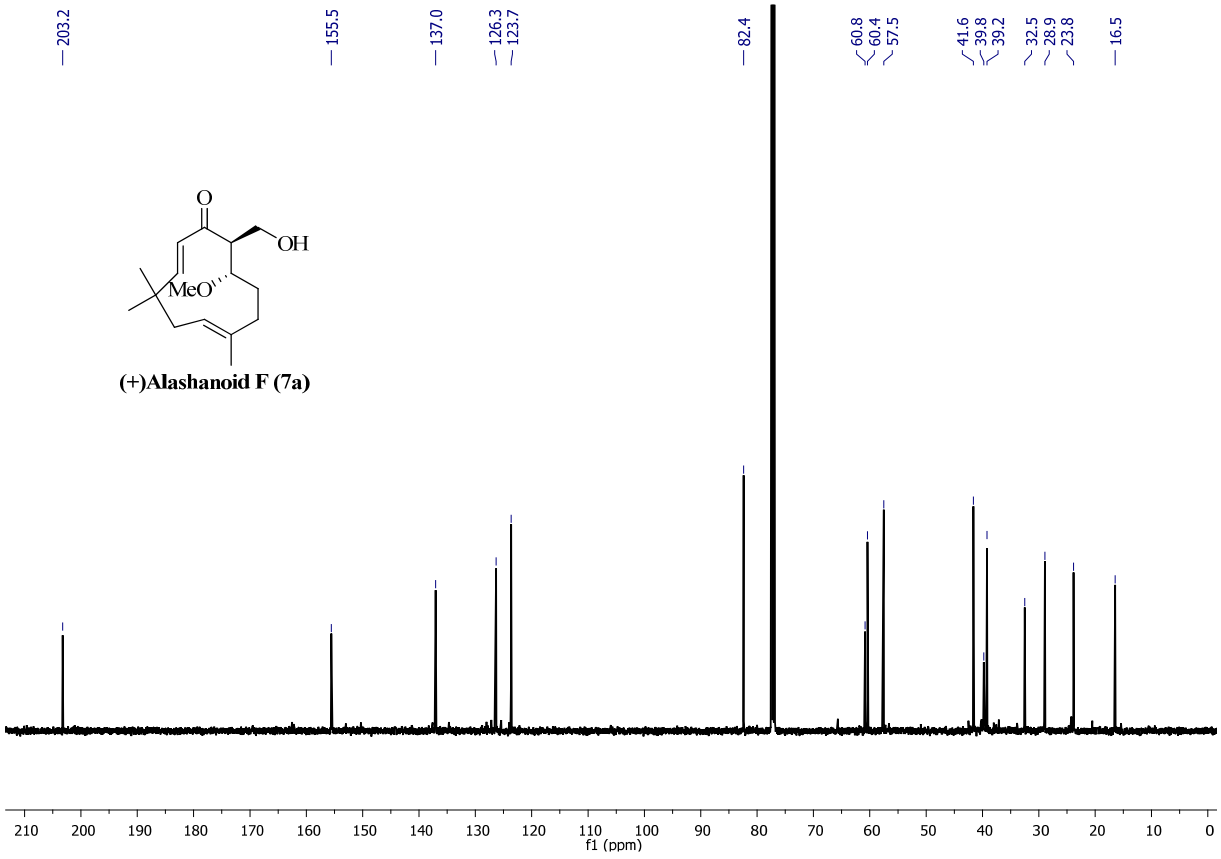
PDA Ch1 254nm 4nm

Peak#	Ret time	Conc	area	Height	Area (%)
1	22.826	100.00	20672561	543504	100

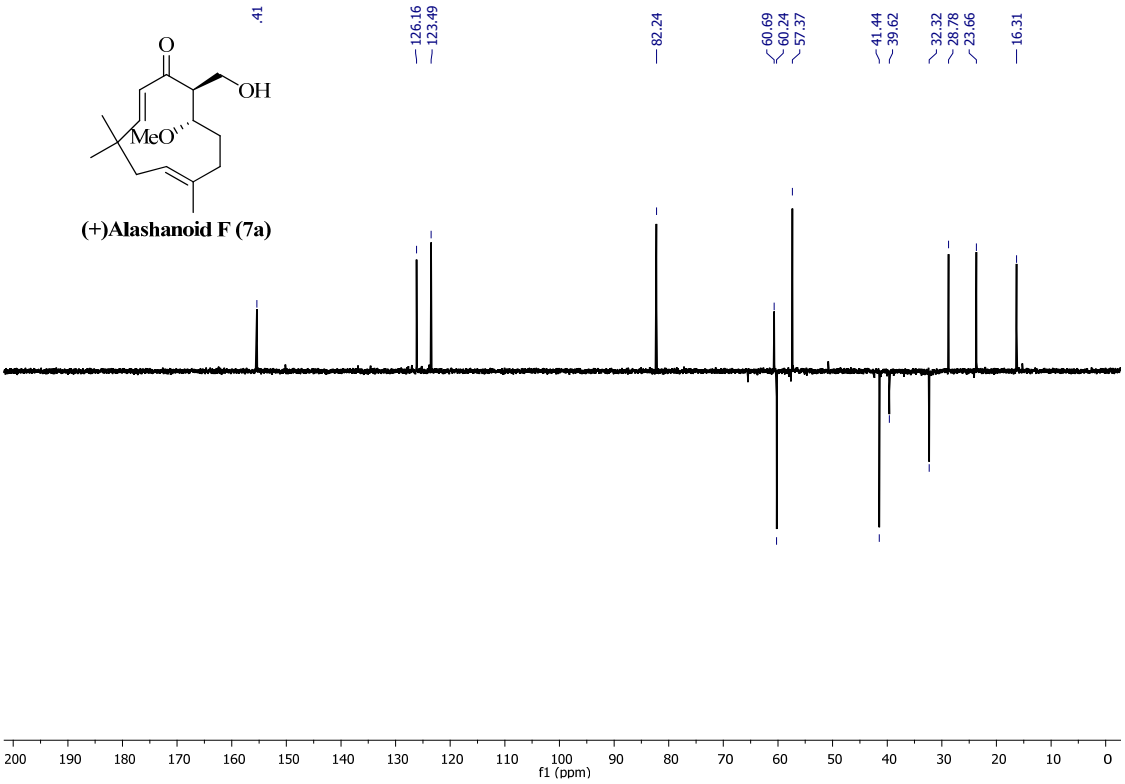
12.4: ^{1}H NMR of (+)-alashanoid F (7a) (500MHz, $CDCl_3$)



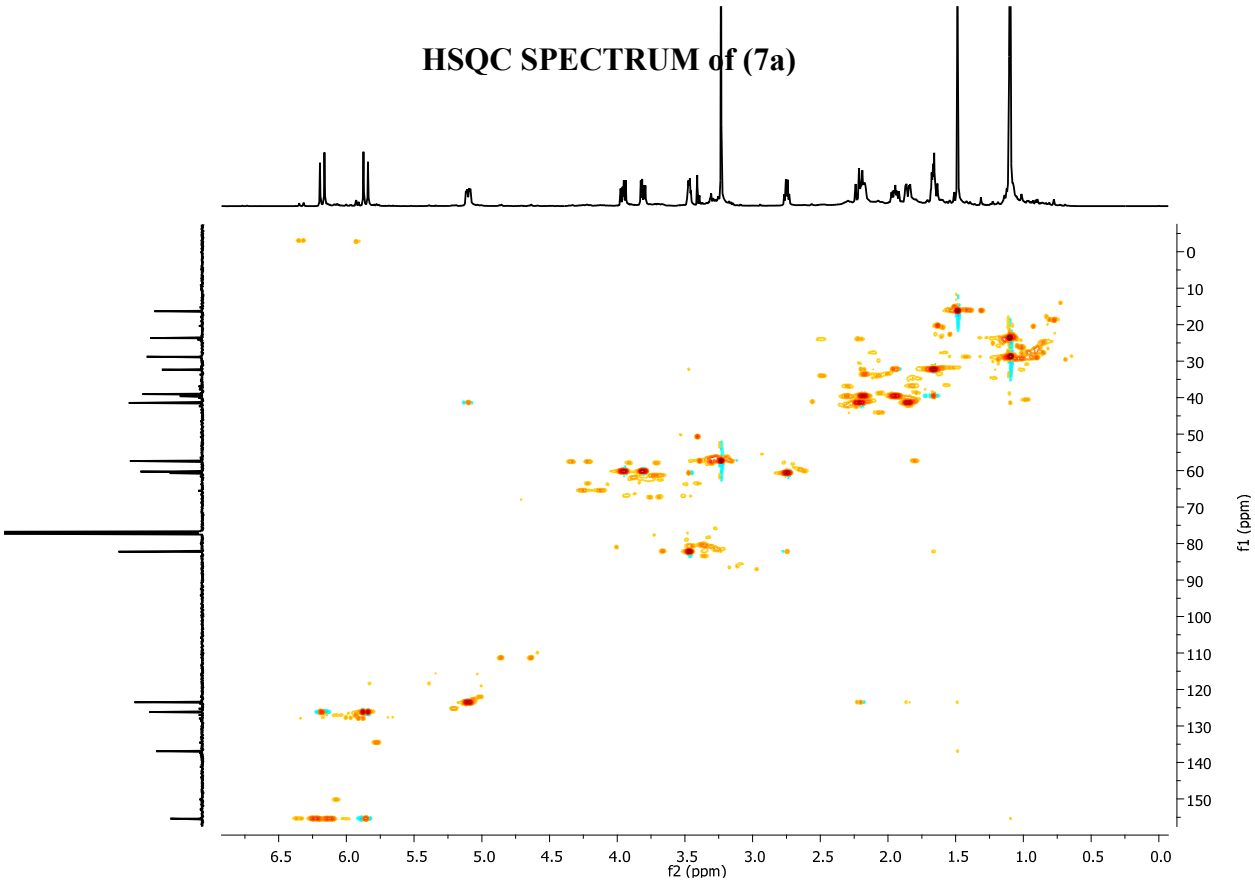
12.4: ^{13}C NMR of (+)-alashanoid F (7a) (125MHz, $CDCl_3$)



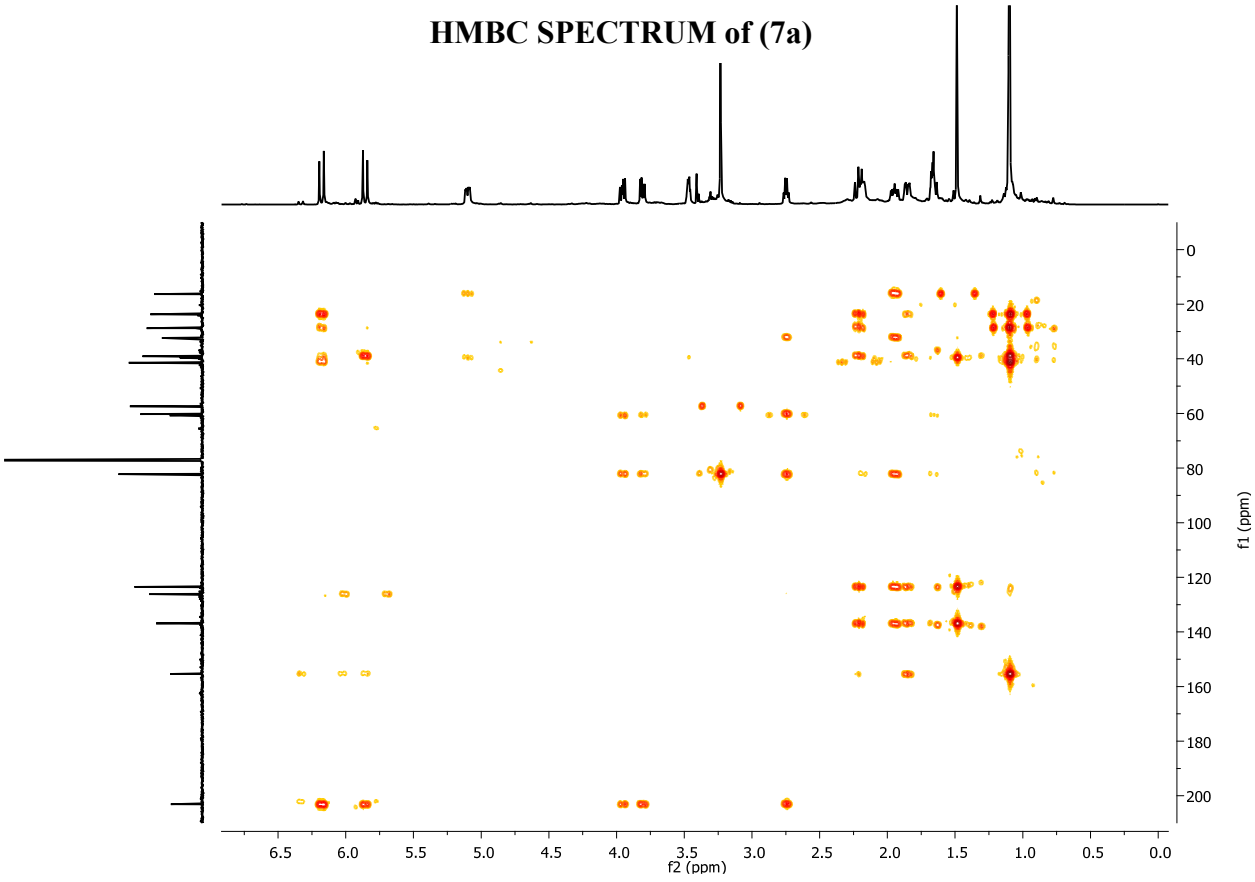
12.4: DEPT-135 NMR of (+)-alashanoid F (7a) (125MHz, $CDCl_3$)



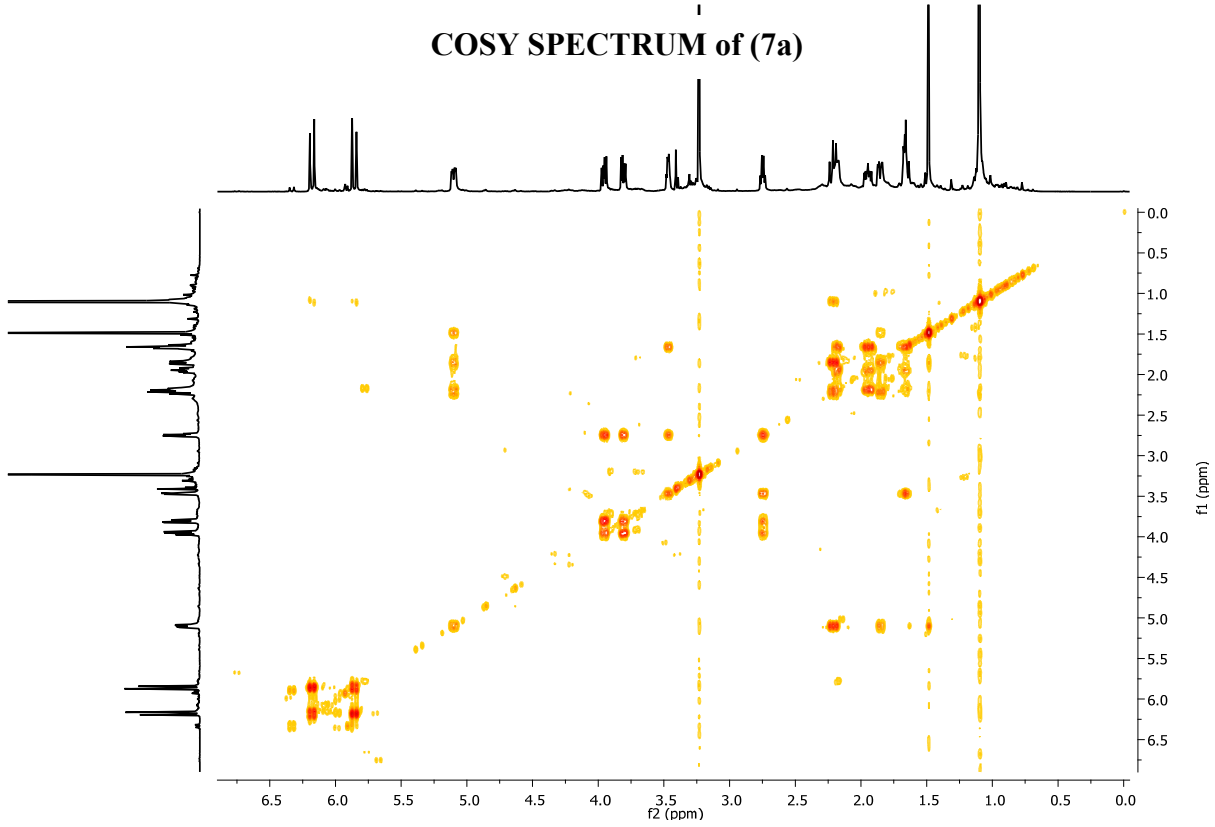
HSQC SPECTRUM of (7a)



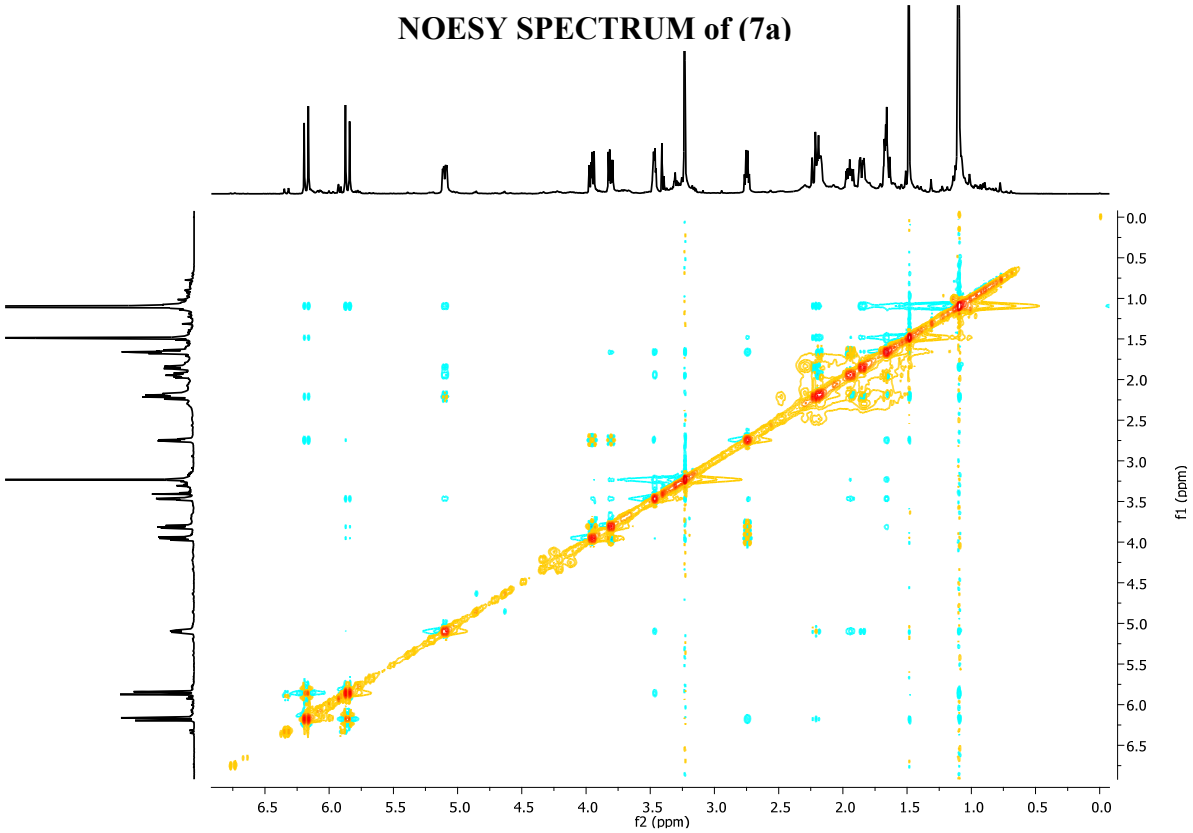
HMBC SPECTRUM of (7a)



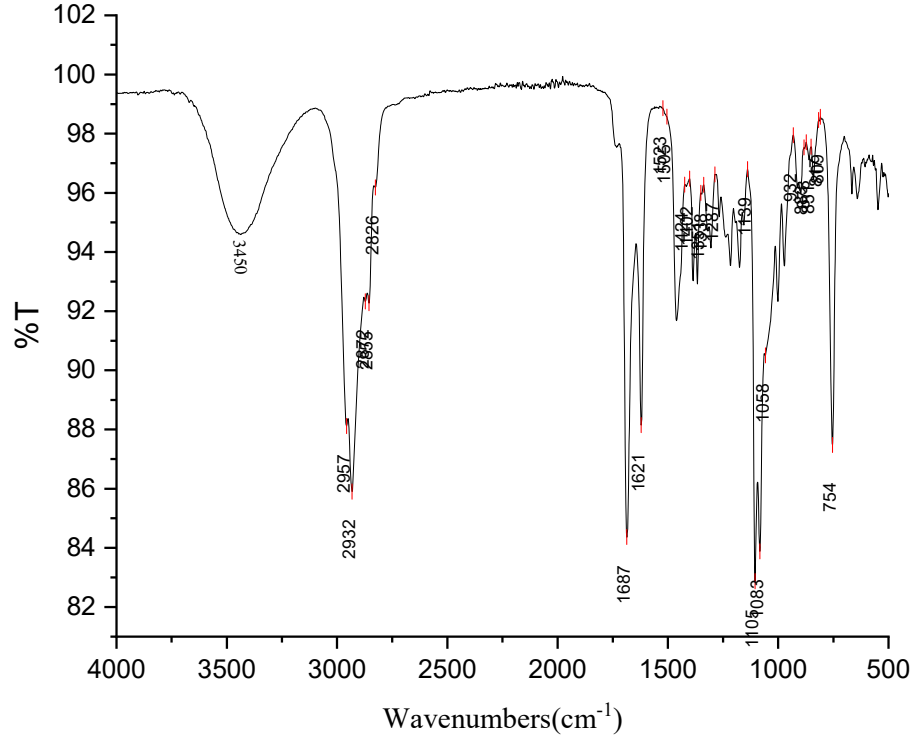
COSY SPECTRUM of (7a)



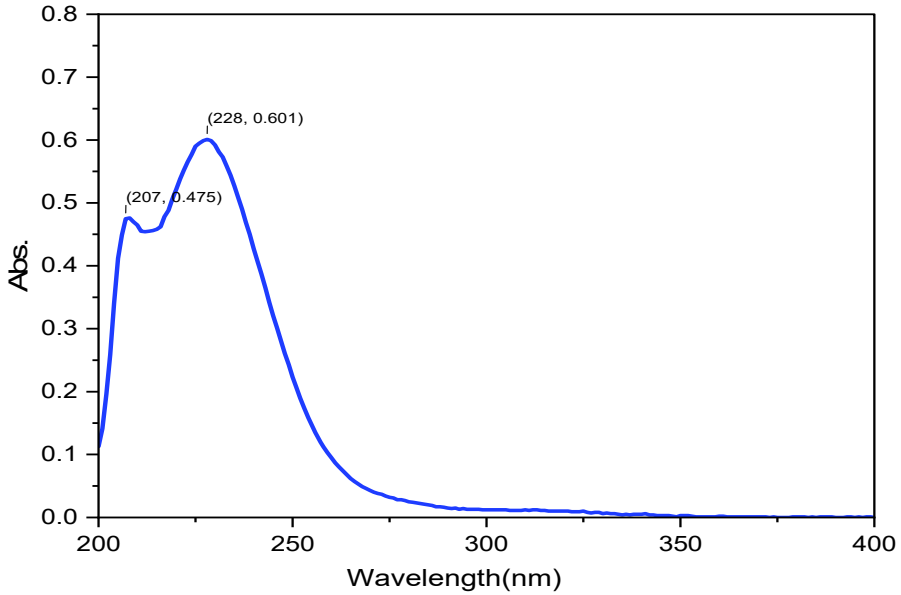
NOESY SPECTRUM of (7a)



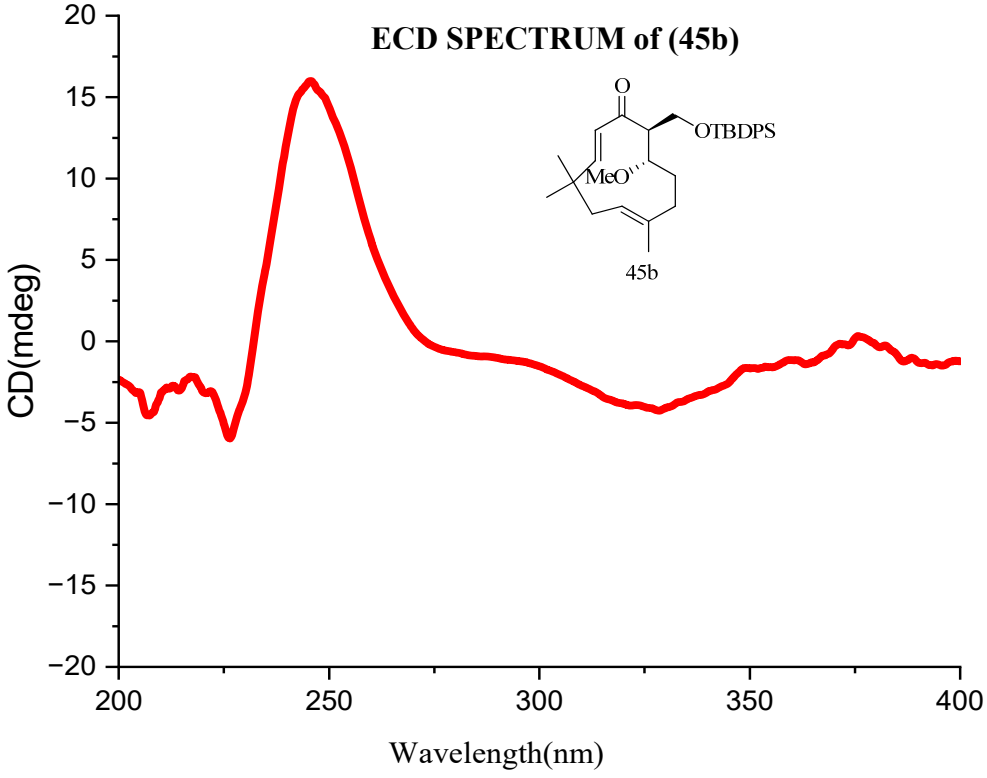
IR SPECTRUM of (7a)

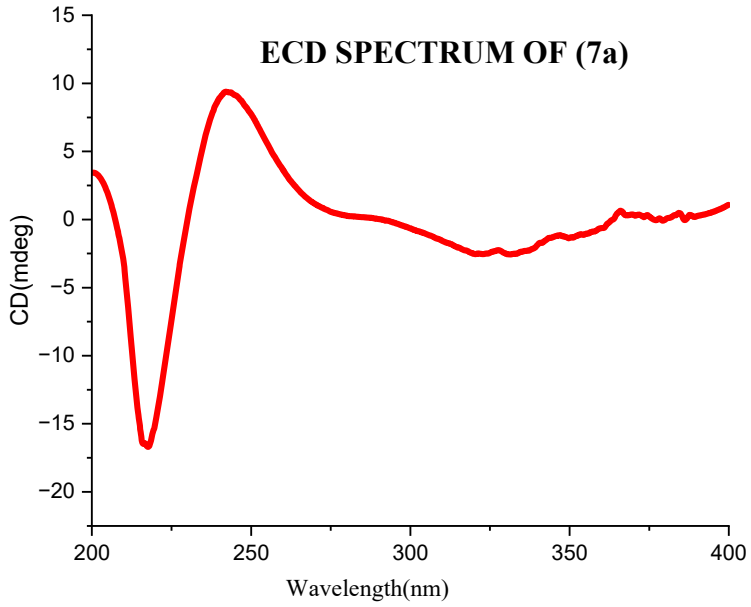


UV SPECTRUM of (7a)



ECD SPECTRUM of (45b)

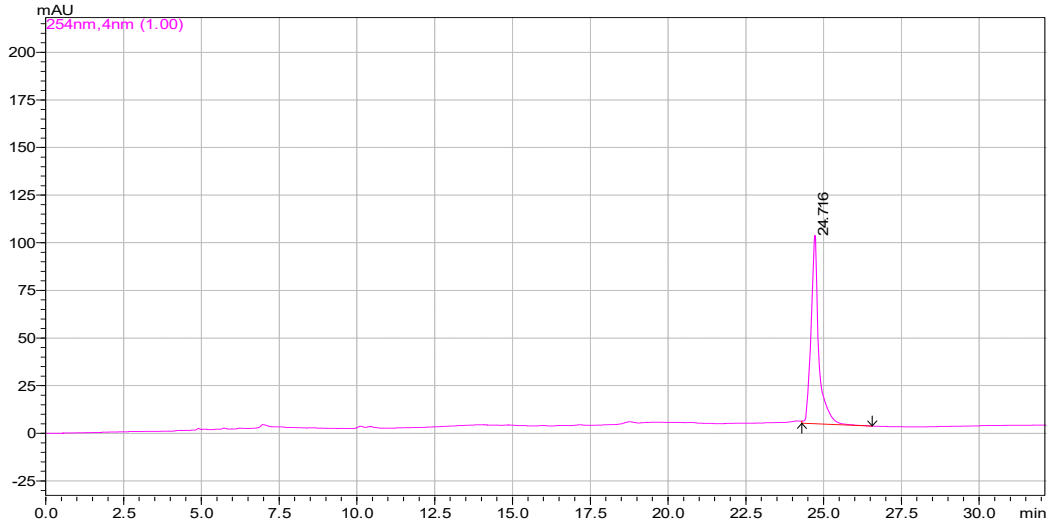




HPLC of Alashanoid F (7a)

Column: CHIRALPAK IC; Flow rate: 0.8 ml/min

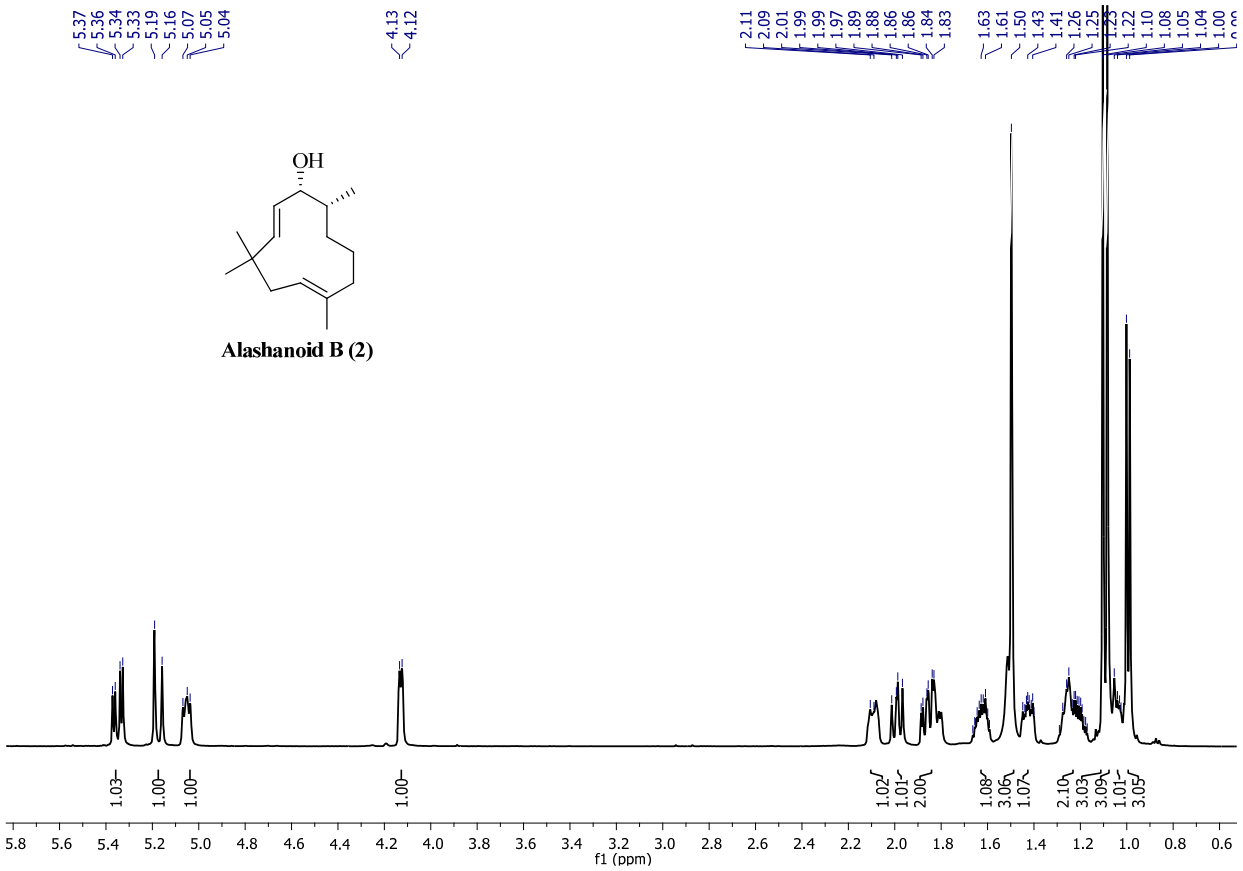
Mobile phase: 10:1; hexane:IPA; Injection volume: 10µL



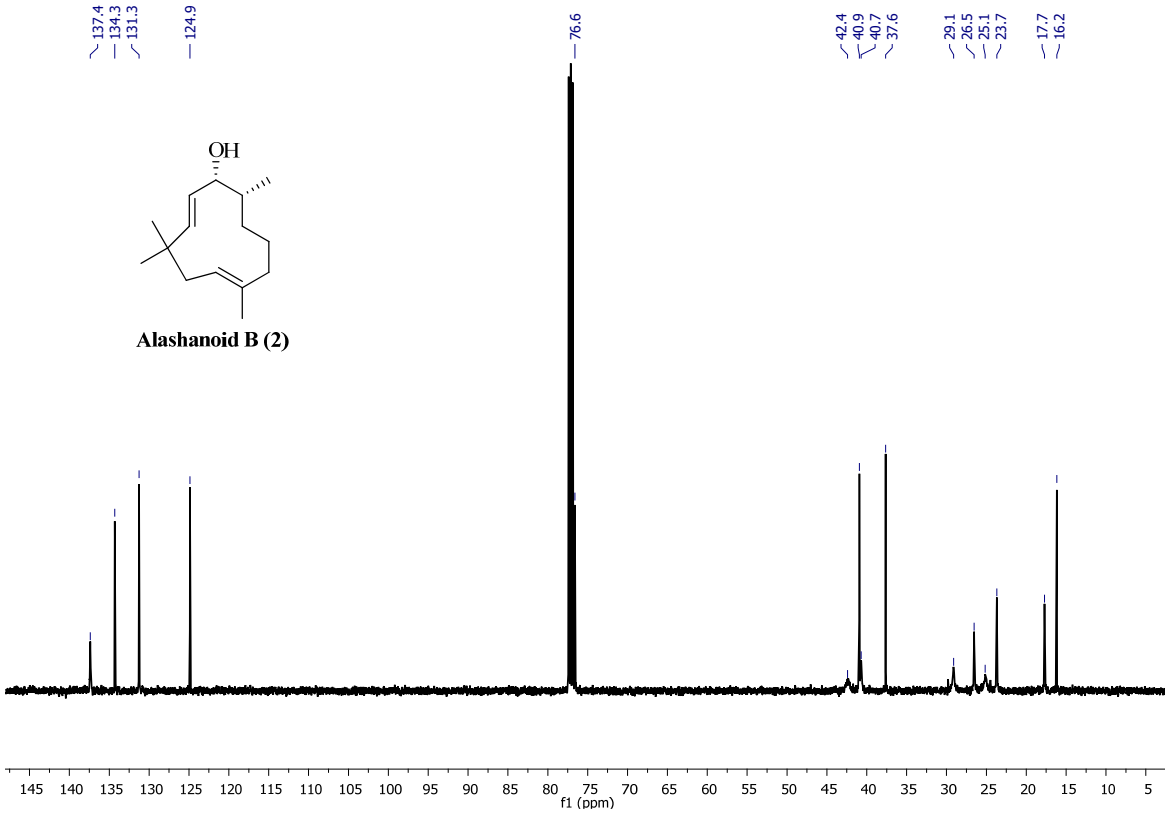
PDA Ch1 254nm 4nm

Peak#	Ret time	Conc	area	Height	Area (%)
1	24.716	100.00	1693663	98877	100

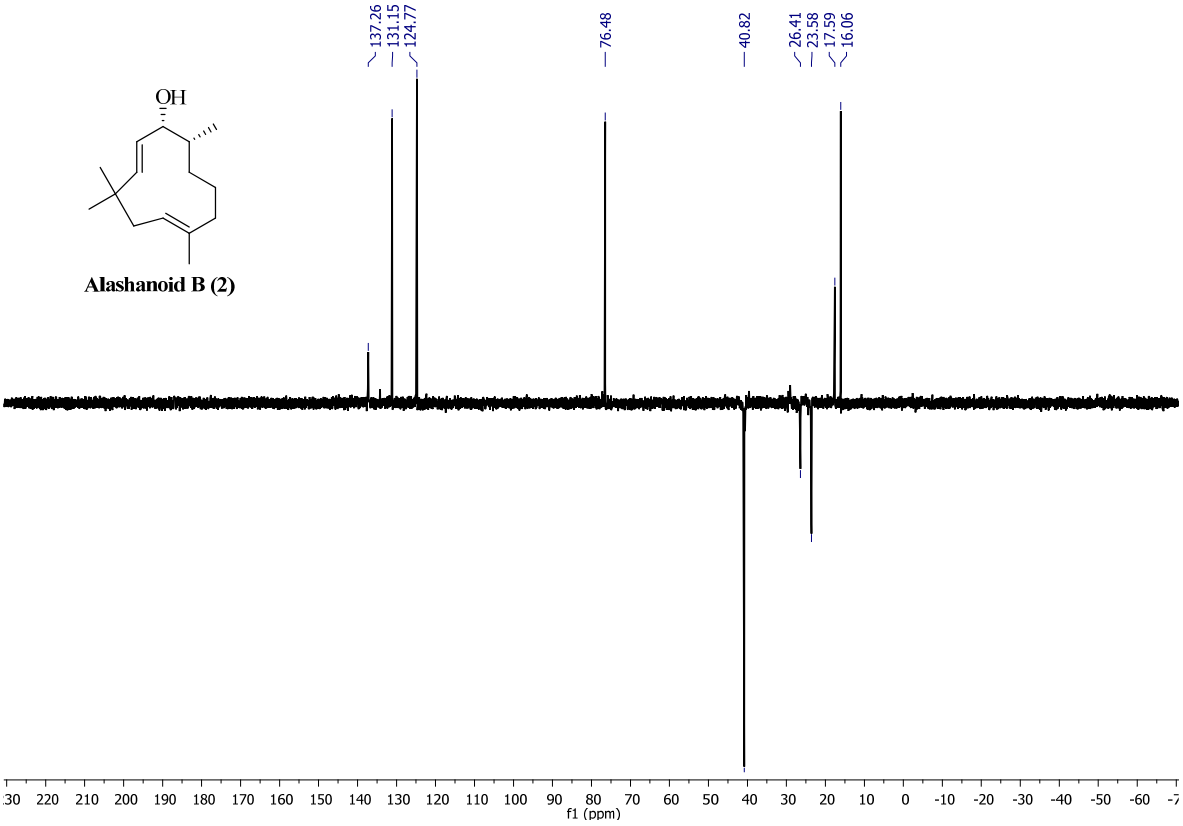
12.5: ^{1}H NMR of Alashanoid B (2) (500MHz, $CDCl_3$)

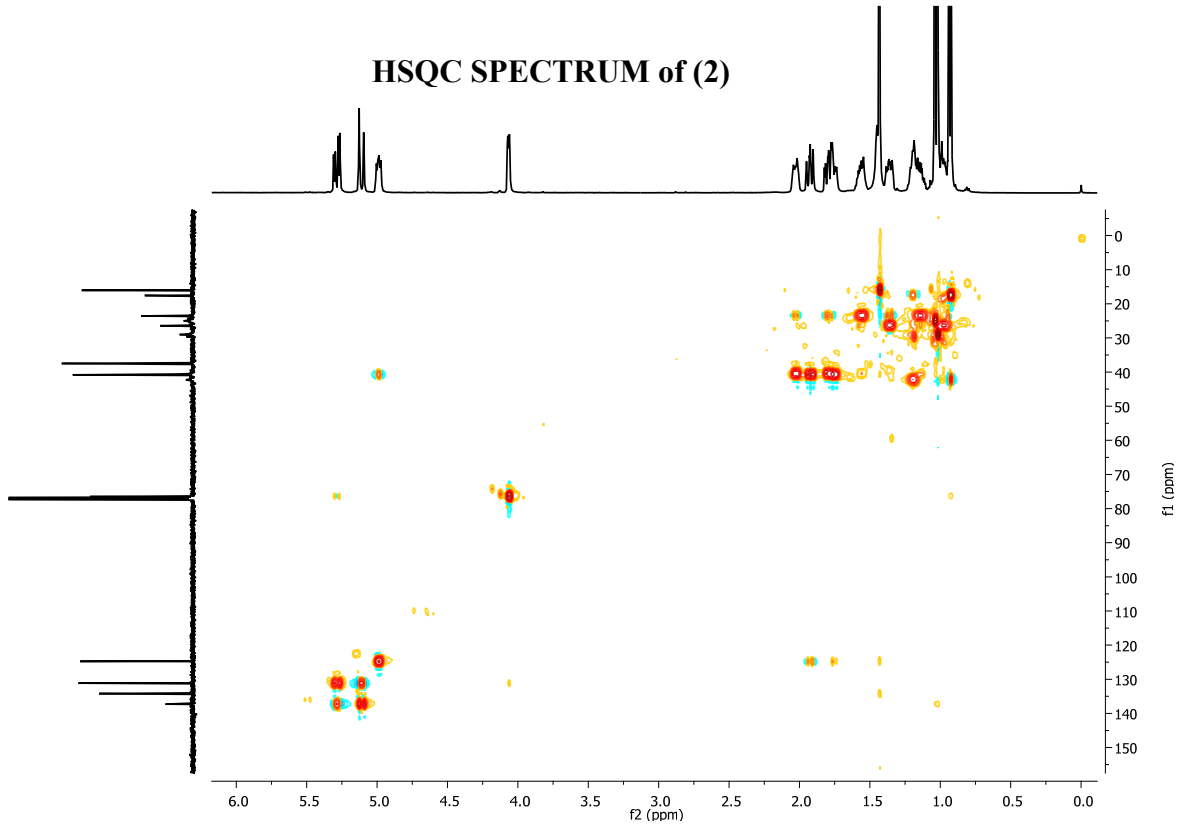


12.5: ^{13}C NMR of Alashanoid B (2) (125MHz, $CDCl_3$)

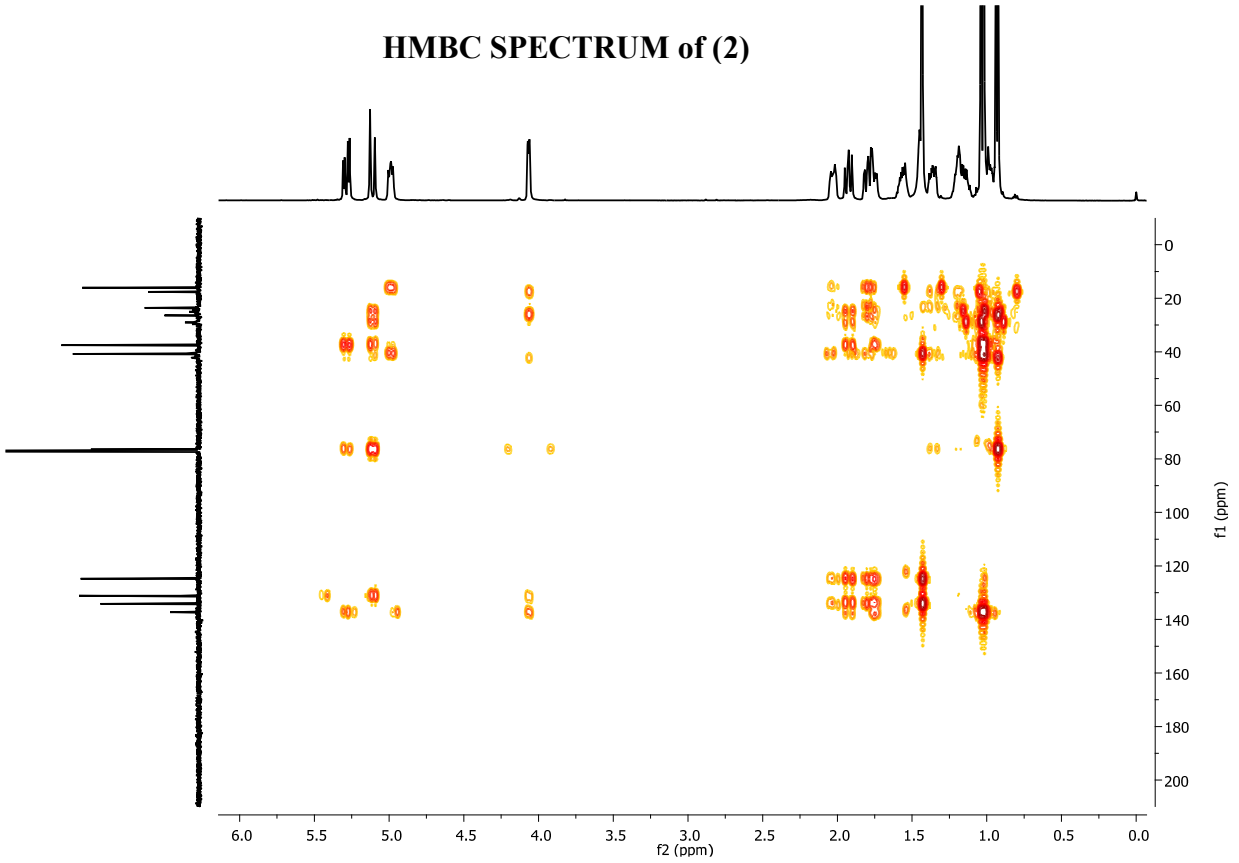


12.5: ^{13}C NMR of Alashanoid B (2) (125MHz, $CDCl_3$)

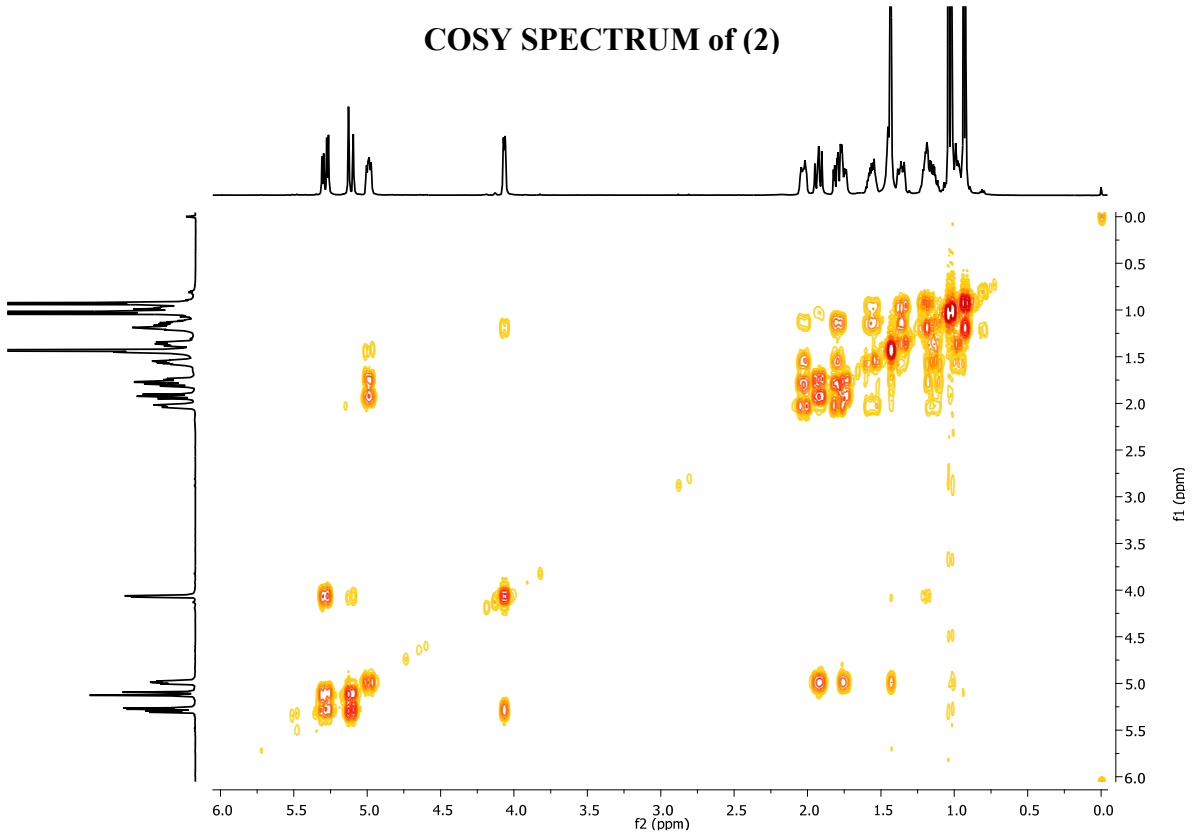




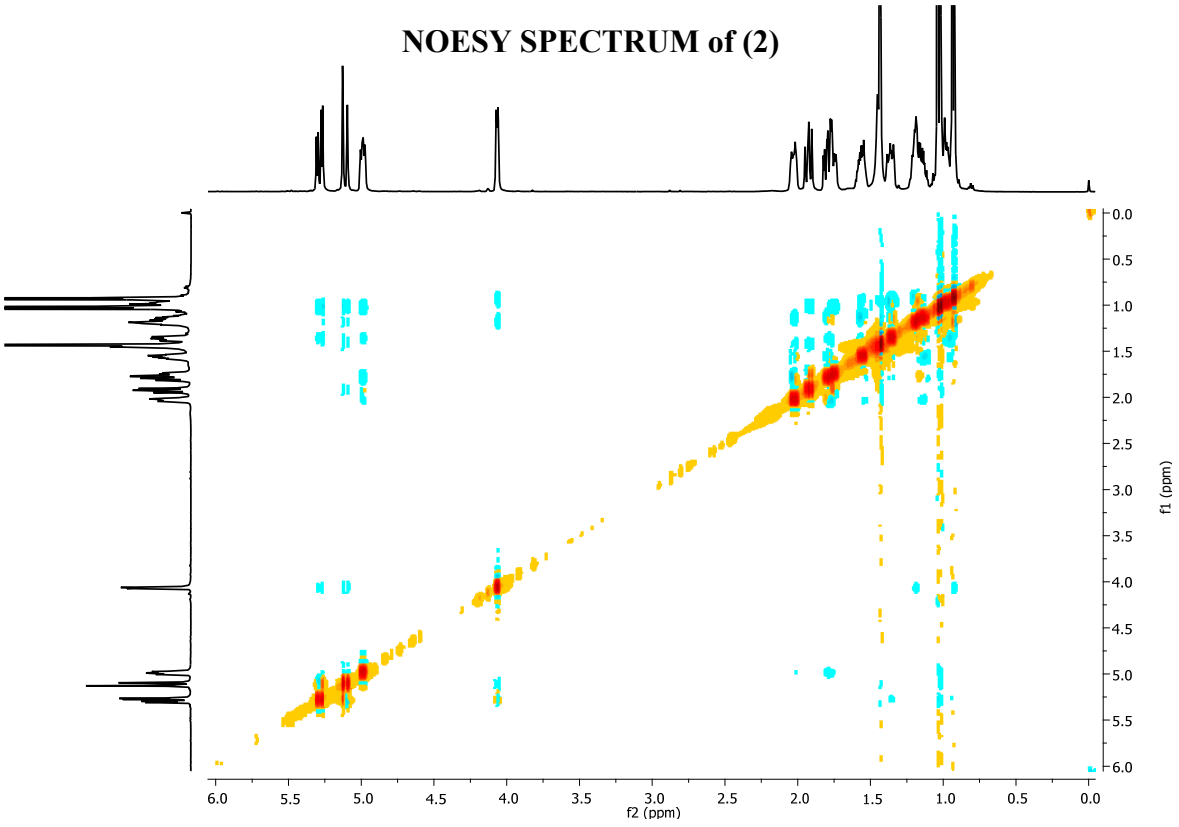
HMBC SPECTRUM of (2)



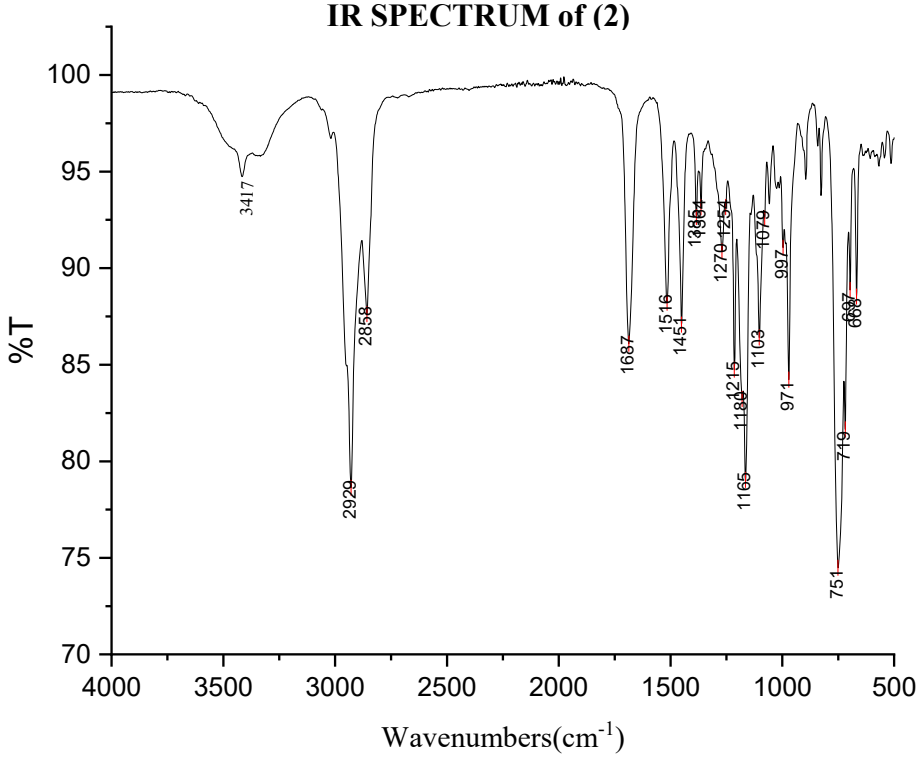
COSY SPECTRUM of (2)



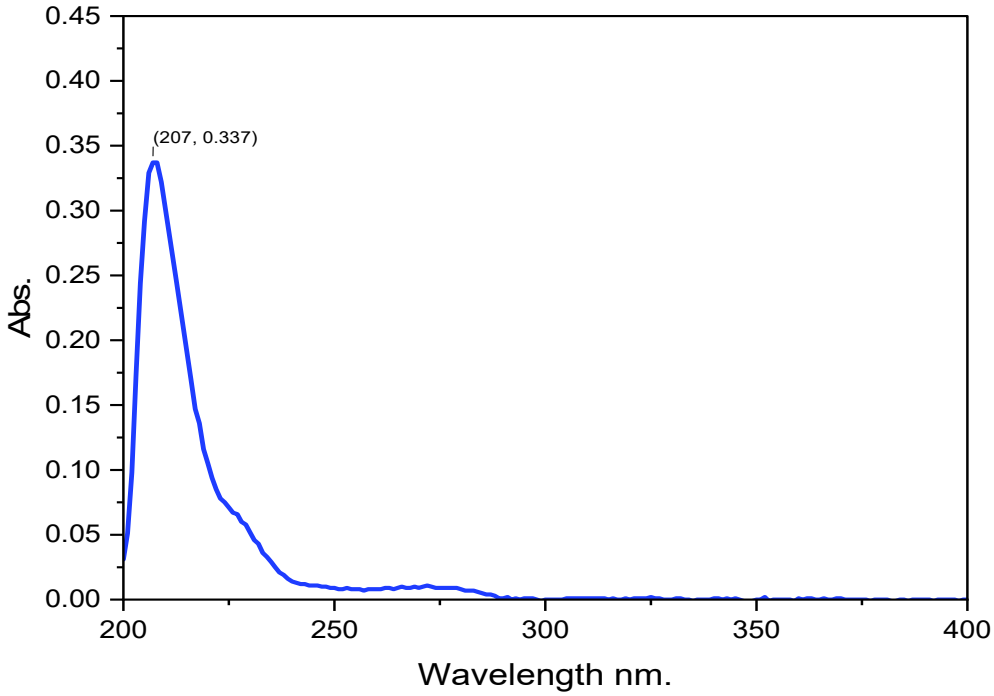
NOESY SPECTRUM of (2)



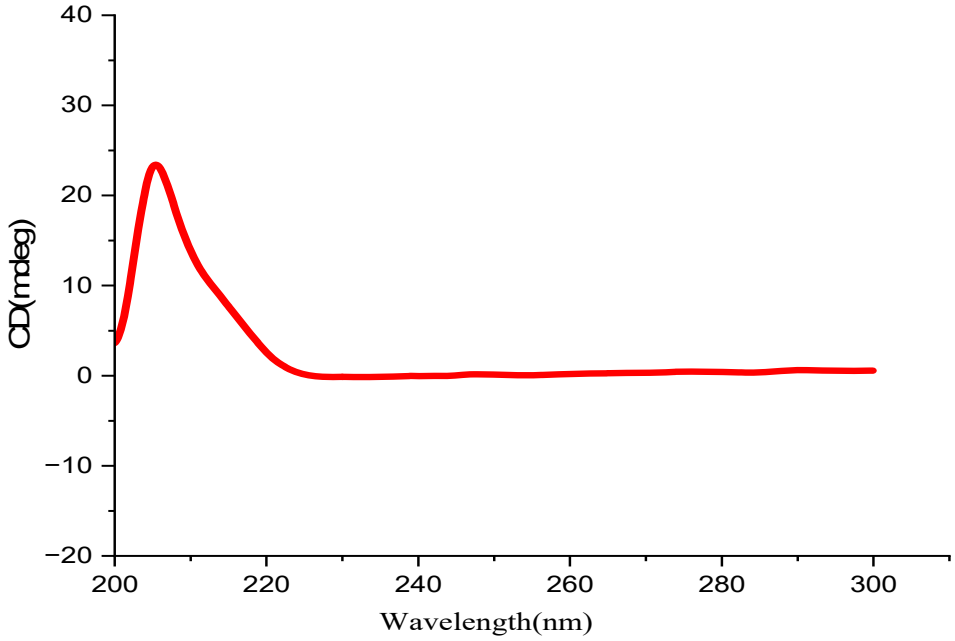
IR SPECTRUM of (2)



UV SPECTRUM of (2)



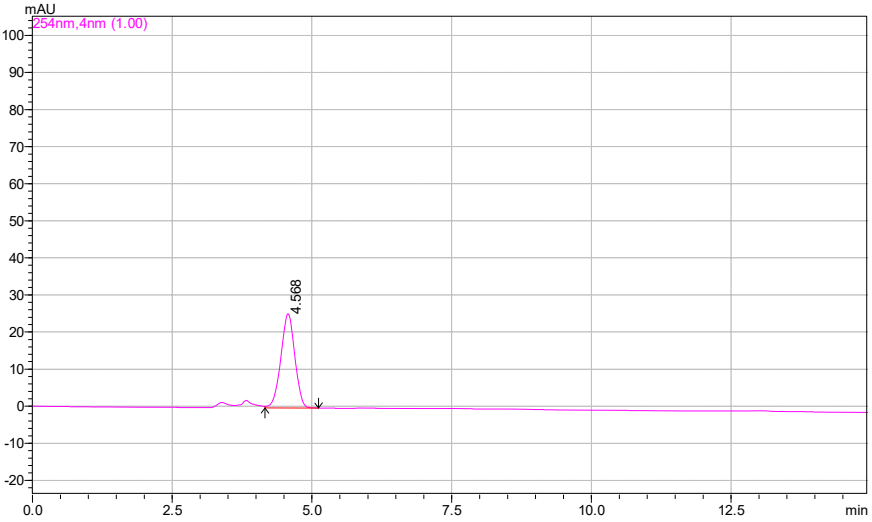
ECD SPECTRUM of (2)



HPLC of Alashanoid B (2)

Column: CHIRALPAK IC; Flow rate: 1.0 ml/min

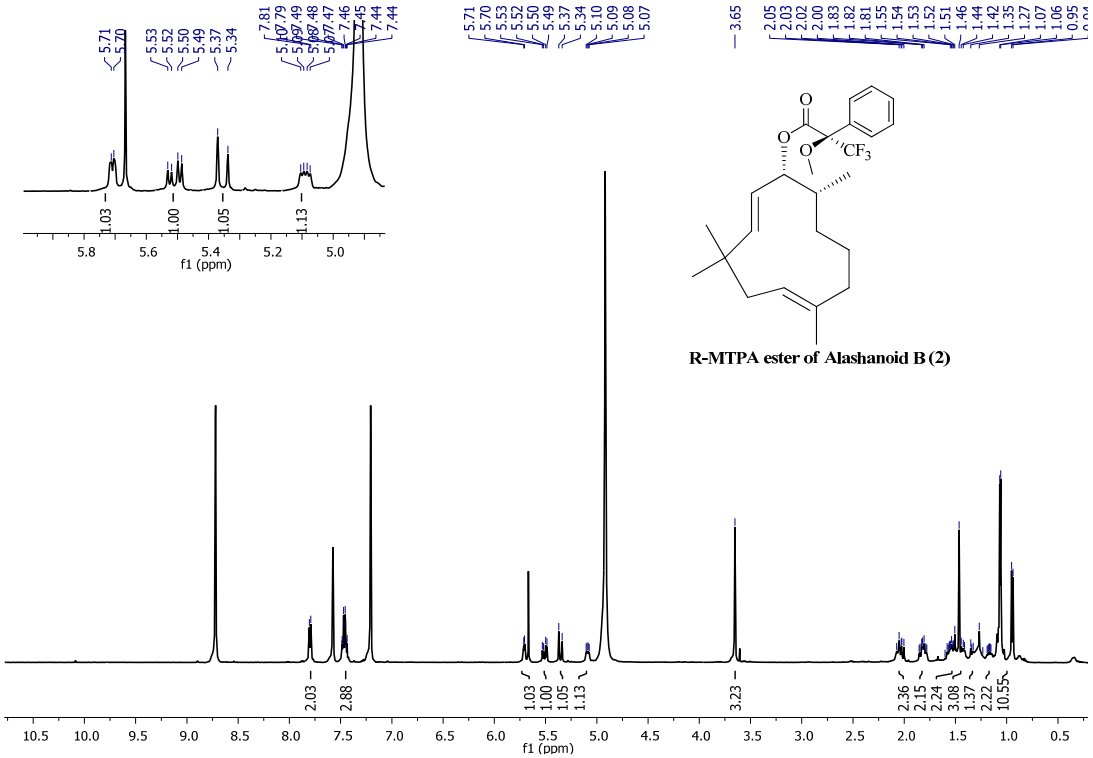
Mobile phase: 50:1; hexane:IPA; Injection volume: 10µL



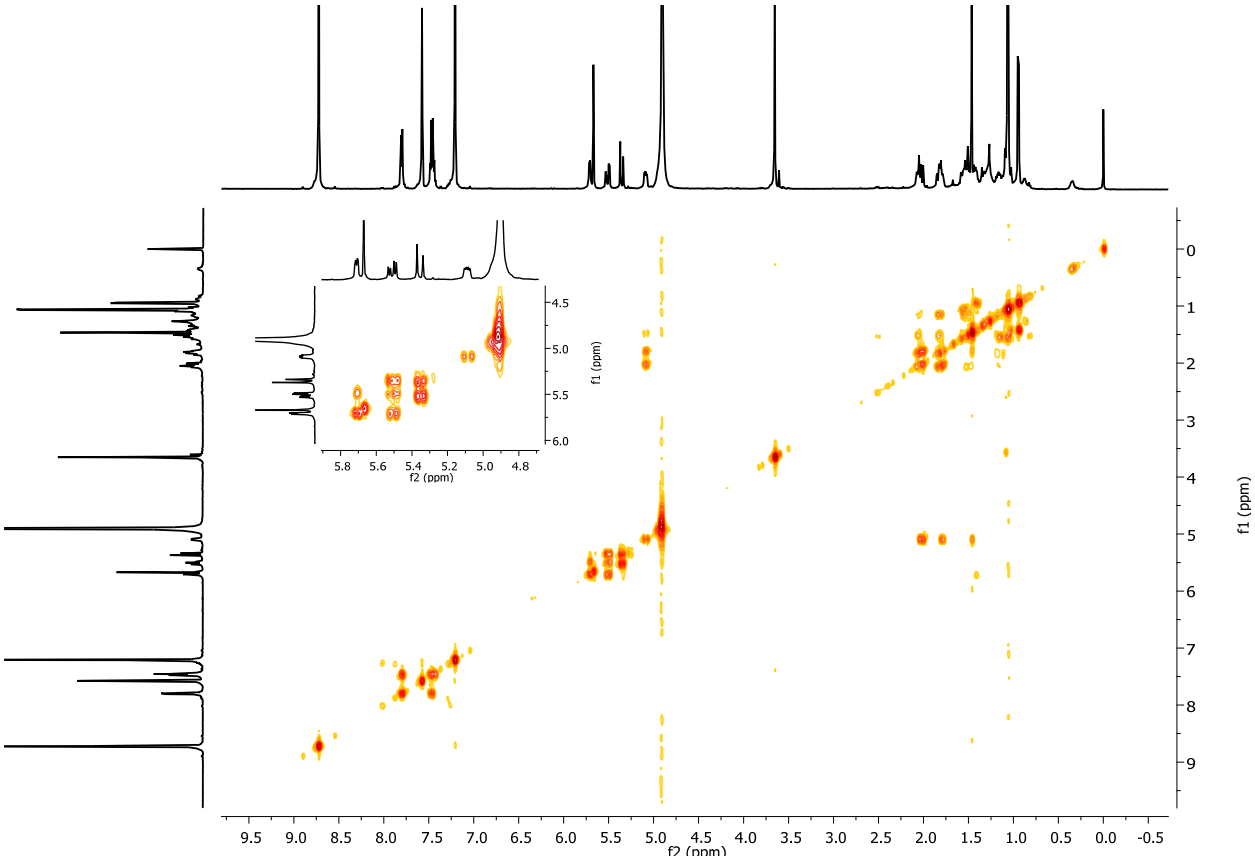
PDA Ch1 254nm 4nm

Peak#	Ret time	Conc	area	Height	Area (%)
1	4.568	100.00000	440960	25425	100

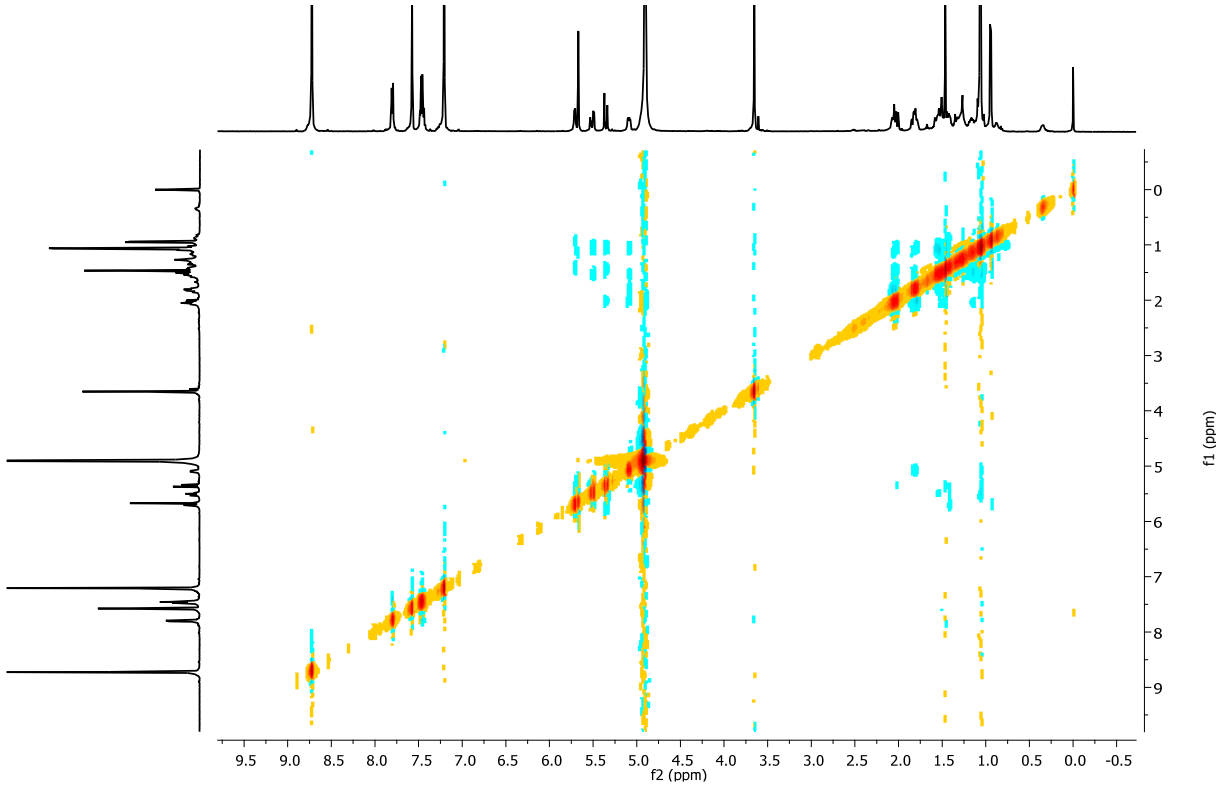
12.6: R- Moser ester of Alashanoid B (2) (500MHz, Pyridine d_5):



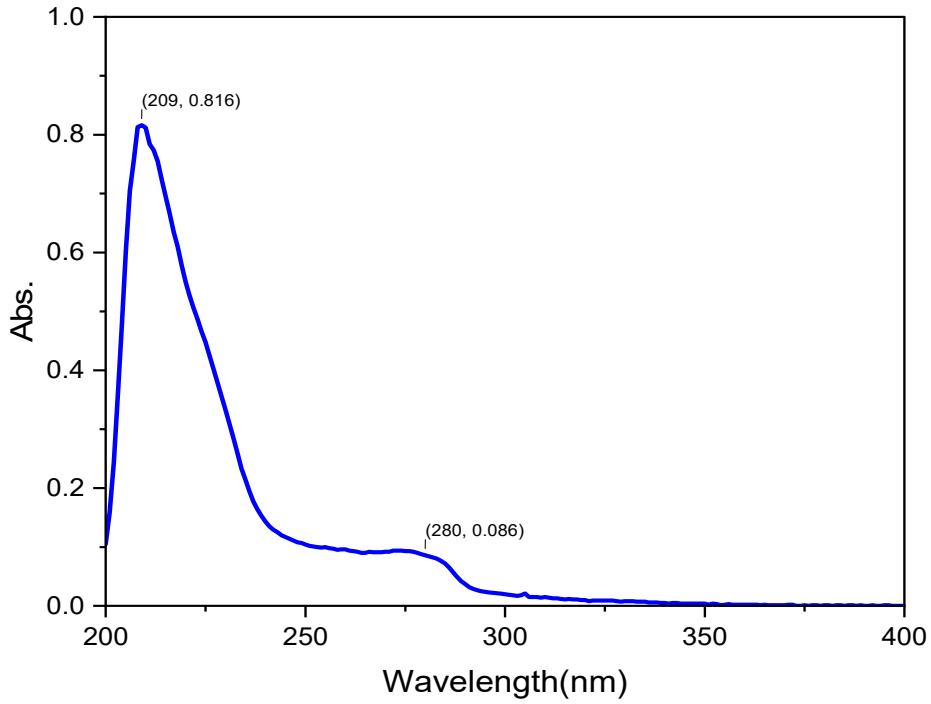
COSY spectrum of *R*-MTPA ester of 2 in Pyridine-d_5 (500 MHz)



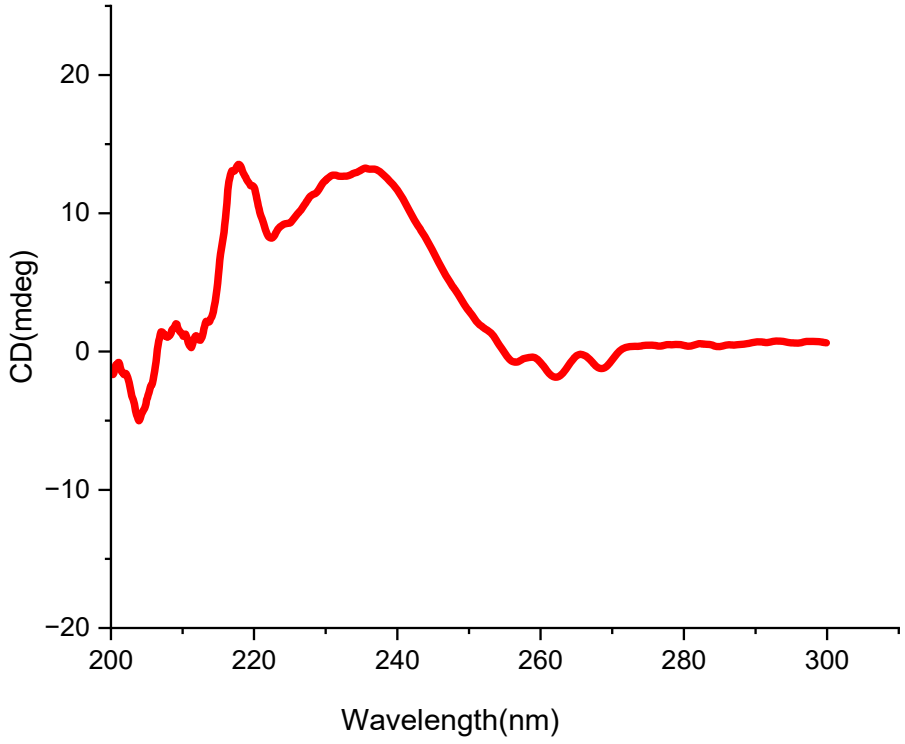
NOESY spectrum of *R*-MTPA ester of 2 in Pyridine-d_5 (500 MHz)



UV SPECTRUM of *R*-MTPA ester of 2



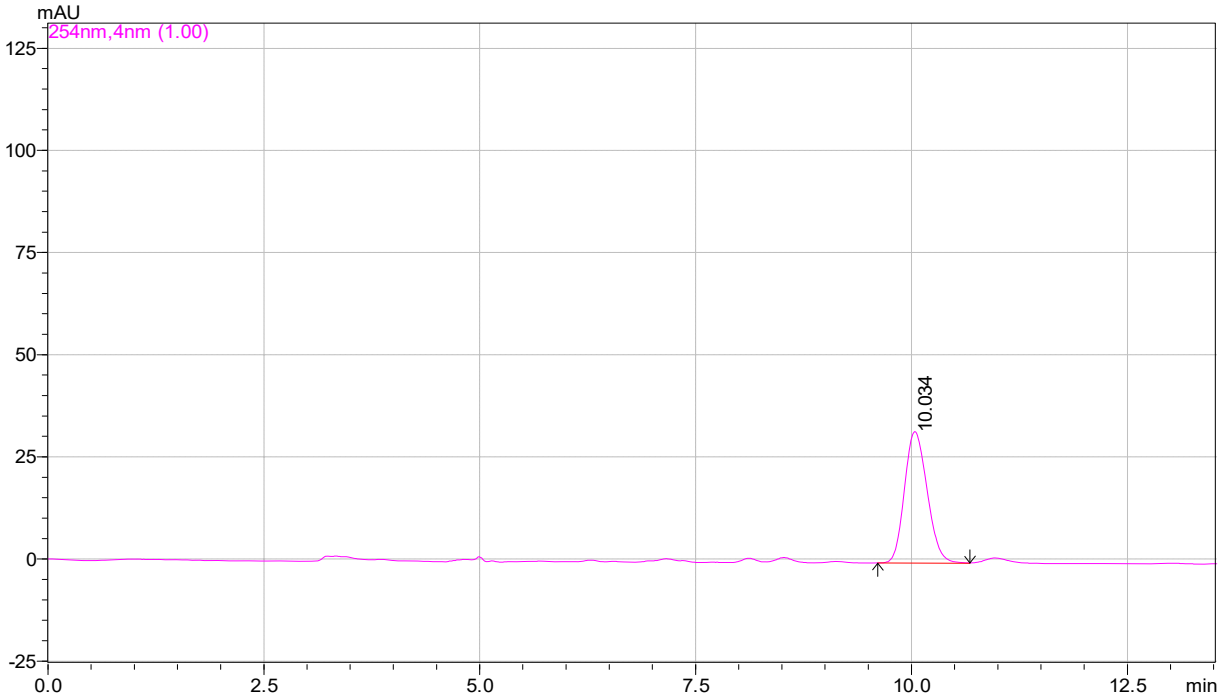
ECD SPECTRUM of *R*-MTPA ester of 2



HPLC OF *R*-MTPA ester of 2

Column: CHIRALPAK IA; Flow rate: 1.0 ml/min

Mobile phase: 100:1; hexane:IPA; Injection volume: 10µL



PDA Ch1 254nm 4nm

Peak#	Ret time	Conc	area	Height	Area (%)
1	10.034	100.00000	589356	32155	100